

PETROL  
AND  
PETROLEUM SPIRITS

# PETROL AND PETROLEUM SPIRITS

*A DESCRIPTION OF THEIR SOURCES,  
PREPARATION, EXAMINATION  
AND USES*

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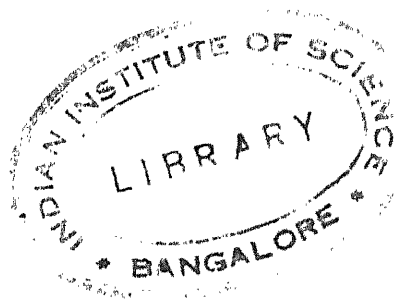
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TO MY PARENTS THIS LITTLE WORK  
IS AFFECTIONATELY DEDICATED  
W. E. G.



## PREFACE

THE subject of Petroleum Technology has become of such importance, and the uses to which Petroleum products are being put are so numerous, that there has arisen an unprecedented demand for text books and works of reference, on the many phases of the subject. The classic work of Sir Boverton Redwood on Petroleum has become, and will remain, a standard text book on the subject in general, and such volumes as this written by one who has had actual experience both in the oilfield laboratory and in the routine work of testing imported petroleum products cannot fail to be of value to those who are studying the subject and who may perchance have to traverse the same ground. It must be admitted however, that there is a general lack of information as to what "Petrol" really is and what precise qualities should be utilised for the varying purposes to which it is to be applied. How far for instance may a specification differ for the petrol to be used in a stationary engine, a motor car, a tank, or a flying machine? The necessity for securing a homogeneous Petrol for Aviation purposes, although obvious to those who understand the wide range of physical conditions under which the spirit has to be used, is not at present sufficiently realized. To this subject the Author has given well-timed attention and the description of his experience in this direction cannot fail to be of value to producer and consumer alike.

The necessity of adding Petroleum Technology to the curriculum of a modern University has been



recognised by the Royal School of Mines and Birmingham University, and to the student as well as the field chemist the work will surely prove invaluable.

The importance of learning more about Petroleum products generally cannot be too frequently emphasized. Prior to the war, little was known of the toluol or xylol contents of crude oils, and indeed with the great increase which has lately taken place in the world's production of crude oil, the first page has barely been turned in the book which will eventually disclose the composition and possibilities of the products which still await the research of the investigator. Who can say what great chemical industries are not destined to arise in connection with the manufacture of products of which either directly or indirectly crude oil is the foundation.

On the subject of Petrol to which the book pays particular attention the importance of standardization of testing cannot be too seriously considered and efforts are now being made to bring about that standardization of methods which is so desirable.

In no subject is there such a dearth of specialised work as in that of Petroleum Technology, and Captain Guttentag has taken considerable trouble in recording laboratory practice which is certain to be of universal benefit. The work will be acknowledged by those who take an interest in the subject to be highly creditable to the Author.

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## FOREWORD

THE multitudinous uses of Petrol have brought it within the category of common things, but of those who use this substance few have any but the most rudimentary notions of the nature of petrol and its preparation from crude Petroleum.

In the vast literature on Petroleum much information is to be found that is of interest to Petrol users, but the greatest part of that information holds a subordinate position in general treatises on the Technology of Petroleum or is in the form of specialised knowledge unsuitable for the technologist in other industries.

The following chapters contain a description of the sources, preparation, refining and examination of Petrol and it is hoped that they may be found interesting, if not useful, to automobile and aeronautical engineers and others who have to deal with Petrol.

References have been given wherever possible to assist in the closer study of Petrol so that the book may be of service also to the student of Petroleum Technology.

The Author wishes to express his gratitude to Capt. T. S. Masterson, D.S.O., M.Inst.P.T. and to Mr V. C. Illing, B.A. (Cantab.), F.G.S., for the kind and helpful suggestions they have been good enough to offer and of which full advantage has been taken.

W. E. G.

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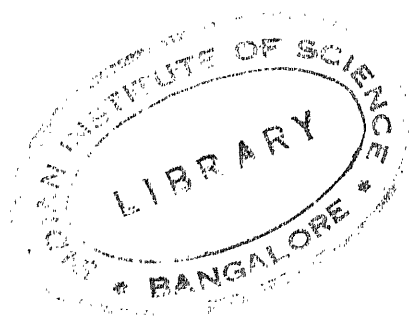
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# PETROL AND PETROLEUM SPIRITS

## CHAPTER I

### INTRODUCTORY

PETROLEUM SPIRIT is a general term covering all the more volatile products obtained from crude petroleum.

The most familiar of these products is the portion used as fuel in the internal combustion engine, this is usually known as Petrol.

In America and Canada the family name for all the light petroleum distillates is naphtha and the fuel is known as gasoline.

On the Continent, benzine is the general term; petrol being known as Essence.

For the purposes of the present work the terms petrol and petroleum spirit have been adhered to as far as possible but the synonyms benzine, naphtha and gasoline have been introduced where they appeared more appropriate.

It must be understood that the commercial spirits obtainable on the market present very wide variations in composition and properties. The factors involved in these variations being:

1. Origin of raw material.
2. Method of manufacture, and,
3. Features desired in the finished product.

It will therefore be recognised that petrol and petroleum spirits should be regarded as a class of substances rather than as a definite material.



Petrol is obtained commercially by the following processes:

1. Distillation from Crude Petroleum.
2. Distillation from Shale Oil.
3. Condensation of Natural gas (Casing-head gas), and,
4. "Cracking" of heavier Petroleum Distillates.

The variations in the properties of the resultant products from the four processes mentioned above will be dealt with under their separate headings.

Since crude petroleum is by far the most prolific source of petrol to-day, it will be well to consider it in rather more detailed form than the other sources which, at the present time, are hardly more than supplementary.

Petroleum is very widely distributed throughout the world. Although the known oilfields are restricted to a few parts of the world only, in most countries traces of crude oil are found. The countries richest in economic deposits in order of importance are: America, Russia, Galicia, Roumania and Dutch East Indies. In many other countries petroleum industries are growing up as witness Mexico, Peru, Trinidad, etc.

It is interesting to observe that the first recognition of the value of petroleum came not through its combustible properties, but by means of its use as a medicine and a lubricant. In fact, in some cases the lighter spirit was actually burnt away, leaving the viscous dark oil as the desired result.

## CHAPTER II

### PETROLEUM

#### (a) Characteristics

PETROLEUM as found in nature is a liquid lighter than water, usually opaque in mass but of a dark brown colour in thin layers by transmitted light, and often dark green by reflected light. The exceptions are numerous, some oils being more black than brown, e.g., Mexican, and some are yellow transparent liquids. Whereas the former type may have lost the lighter and more volatile portions of the original oil, the latter are probably produced by filtration through decolourising earthy material. Some Roumanian, Californian and Italian crude oils are of this light straw colour, but it is noteworthy that oils of this type are not abundant and that the general description above holds for nearly all crude oils that are handled commercially.

The smell of some oils is pleasant as is the case with the Italian light coloured oil, which has a distinctive aromatic odour. There are other oils, however, in which the smell is most unpleasant. This is frequently coincident with the presence of sulphur and nitrogen compounds, but is not necessarily a guide as to the presence of these bodies.

The specific gravity of petroleum usually falls between the limits 0.780–1.00, most figures being in the neighbourhood of 0.860 to 0.900.

Petroleum is truly a mixture of substances; gaseous, liquid and solid. Natural gas which usually

accompanies the oil from the well is held in solution in the crude oil and is liberated during the refining process of distillation.

Paraffin wax which is a solid substance when pure and at ordinary temperatures is likewise soluble in the crude oil. The proportion of these gaseous and solid constituents is not constant, it varies from one type of oil to another, and even in oils from neighbouring wells drawing from the same sources.

The chemical composition of petroleum opens up a vast field of study which is as yet not fully explored.

TABLE I.

*Elementary composition of various Petroleums.*

| Source              | Car-<br>bon | Hydro-<br>gen | Oxy-<br>gen | Sul-<br>phur | Nitro-<br>gen | Authority       |
|---------------------|-------------|---------------|-------------|--------------|---------------|-----------------|
| Pennsylvania        | 86.06       | 13.89         | ...         | 0.06         | ...           | Engler          |
| Oil City, Pa.       | 85.80       | 14.04         | ...         | ...          | ...           | Mabery          |
| Findley, Ohio       | 84.57       | 13.62         | 0.98        | 0.72         | 0.11          | Mabery          |
| Lima, Ohio          | 85.00       | 13.80         | ...         | 0.60         | 0.68          | Rakusin         |
| Beaumont, Texas     | 85.05       | 12.30         | ...         | 1.75         | ...           | Richardson      |
| Ventura, Cal.       | 84.00       | 12.70         | 1.20        | 0.40         | 1.70          | U.S. Government |
| Wasatch Range, Utah | 86.86       | 11.89         | 0.59        | 0.64         | 0.02          | Mabery & Byerly |
| Grossny, 0.906      | 86.41       | 13.00         | 0.40        | 0.10         | 0.07          | Charitschkoff   |
| Grossny, 0.850      | 85.95       | 13.00         | 0.74        | 0.14         | 0.07          | Charitschkoff   |
| Tscheleken, 0.8736  | 86.40       | 12.44         | 0.377       | ...          | ...           | Charitschkoff   |
| Campeni-Parjol      | 85.29       | 14.21         | ...         | 0.03         | ...           | Edeleanu and    |
| Bustenari (Prahova) | 86.30       | 13.32         | ...         | 0.18         | ...           | Tanasescu       |
| Variations          | 79.5        | 9.6           | 0.1         | 0.01         | 0.02          | } Holde         |
|                     | to          | to            | to          | to           | to            |                 |
|                     | 88.7        | 14.8          | 6.9         | 2.2          | 1.7           |                 |

A very large number of compounds of carbon and hydrogen combined in various proportions, with, occasionally, compounds of carbon, hydrogen and nitrogen, or carbon, hydrogen and oxygen, or carbon, hydrogen and sulphur, are the main constituents of petroleum. Sometimes hydrogen sulphide or elementary sulphur are contained in solution.

The sulphur, as stated above, may be in one or more of three forms: elementary, i.e., uncombined, or, as hydrogen sulphide, or, as an organic carbon-hydrogen-sulphur compound, in which last case it is removed with more difficulty in the refining process, the oils most afflicted being those of Mexico and Texas.

Further impurities in crude petroleum from the oil field are water and sand and clay in suspension. These are generally removed by settling before treatment in the refinery, but in some cases they entail a tedious process for their elimination.

### (b) Origin

The question of the origin of petroleum is often regarded as a purely theoretical matter of merely academic interest and no industrial importance. Nothing could be more mistaken. The value of sound premises on which the oil prospector can base his conclusions is inestimable.

Once given a true account of the formation of petroleum, the geologist is in a far better position to grasp the circumstances of the migration and the accumulation of economic petroleum deposits:

Many theories have been put forward accounting for the origin of petroleum. Both chemists and geologists have accumulated stores of information and formulated numerous explanations based on their observations in the laboratory and the field respectively. None of the theories is capable of universal application; and it is highly probable that the origin of some deposits is due to causes entirely different from those influencing the birth of others. Nevertheless, among the theories based on geological as well

as chemical observations, as opposed to mere hypotheses, there have arisen explanations that appear to be fairly generally applicable.

Broadly speaking the theories of petroleum genesis may be divided into: (1) Inorganic, and (2) Organic.

### 1. Inorganic Theories

Hydrocarbons such as those found in petroleum are usually known to exist only in association with animal and vegetable matter, they are known, in fact, as organic compounds. When it was found possible to produce these bodies in the laboratory without the intervention of the living organism, be it animal or plant, claims were made that petroleum, the origin of which was clouded in such mystery, must have come into being by a process of generation similar to that by which some of its components had been prepared by the chemist. These arguments, well enough founded, were unfortunately not in accord with observations made by geologists on the field; nevertheless, much evidence has been brought forward in support of this view and the inorganic theory still maintains a certain amount of support at any rate in one of its forms<sup>1</sup>.

The action of water on calcium carbide which produces acetylene, is a familiar example of the reaction held by the inorganic theorists to account for the production of petroleum. Metallic carbides in the bowels of the earth subjected to the action of steam or water would, they maintain, produce ultimately the constituents of petroleum. The association of igneous rocks with petroliferous deposits is further relied upon to uphold this view although it is by no means cer-

<sup>1</sup> Coste, *Trans. Inst. M. M.* xxi. 91-192 (1912).

tain that igneous rocks or volcanic rocks are present in all the oilfields, on the contrary geological experience has pointed definitely to the association of petroleum with water-formed or sedimentary rocks.

The general tendency is to regard the inorganic theory as a stepping stone to a better appreciation of the organic theories.

## 2. Organic Theories

The raw material from which petroleum has been formed, according to the organic theories, is either vegetable or animal matter.

A complete account of the theories mentioned in these pages is outside the scope of this book, but references are here given to what are considered the most reliable sources of detailed information.

Suffice it to say, then, that the vegetable theory accounts for the presence of petroleum in the rocks of the earth's crust as due to a special decomposition probably near the shores of lakes or shallow seas of the vegetation of past ages, such chemical action, be it noted, taking place only under certain given conditions of temperature and freedom from the action of atmospheric oxygen.

Thus a generic relationship is established between the petroleum deposits and the coal seams of the earth. Substantiation to this view is claimed by the fact that in some petroliferous areas coalfields are to be found.

The theory that claims the greater number of adherents to-day, however, maintains an animal origin for the petroleum deposits. This view, stated in detail and in accordance with more recent observations, has been formally enunciated by Engler and

Hofer, though many other workers have come to practically the same conclusions. The older idea that a slaughter *en masse* of land animals or whole seas of fish has given way to the more probable interpretation whereby it is held that the vast quantity of animal material necessary for the formation of the petroleum deposits has been furnished from the lower rather than the higher organisms and that just as our chalk measures are composed of the houses of billions of little shell fish, so the oilfields represent the accumulated animal fats from the micro-organisms of countless ages rearranged and modified in their chemical composition so as to produce the substances of which petroleum is constituted.

One further point is interesting to record. It has been known for a long time that petroleum is capable of rotating a ray of polarised light. It is only within comparatively recent years that Rakusin and Lewkowitsch have pointed out that this rotatory property was probably due to the cholesterol in animal fats and phytosterol of vegetable oils.

The constituents of petroleum which have been synthetically prepared in the laboratories, however, do not show this property of rotation. It is to be concluded therefore that this forms a valuable contribution to the evidence in favour of the organic theory.

The question as to whether the petroleum deposits are of marine or terrestrial origin is of fundamental importance geologically and is as necessary to solve as the problem of the nature of the raw materials from which petroleum itself is derived.

In summing up the evidence at our disposal the following propositions appear to be established.

"1. The evidence available at the present time favours the animal origin of most Petroleum.

2. A certain amount has probably been derived from the fatty portion of plants.

3. The optical and geologic evidence is decidedly against the inorganic origin of Petroleum, but the association of oil and gas with volcanic features in certain fields suggests that there may have been a relationship of cause and effect in the associated phenomena<sup>1</sup>."

### (c) Geological

A consideration of the geology of petroleum is outside the limits of the present work, nevertheless it may be of interest to record a few facts in reference to that science.

A vast amount of knowledge has been accumulated by petroleum geologists on most of the problems of oilfield location and development and although no geologist would claim infallibility for all his surmises it is only a very second rate oil company that would ignore the assistance of the geologist trained in oil-field work.

The geologist to-day, can indicate those geological formations in which petroleum is likely to occur, he can trace those formations through vast tracts of country and point to the areas where the local structure favours the accumulation of oil; then in the selection of his first well site he must take his chance with the 'wild catter,' but the risks of failure have been considerably reduced by the careful elimination

<sup>1</sup> *Petroleum and Natural Gas resources of Canada*, i. 76 (1914). See also on Origin of Petroleum, Cunningham-Craig, *Oil Finding* (Arnold). Dalton, *Economic Geology*, iv. 606 (1909).



of ground proved by observed geological facts, to be almost certainly barren. Further assistance from the geologist and by no means the least important, is gained from his careful records of the development of a field.

These records obtained as the result of proper interpretation of carefully kept well logs and considerations of the rock and fossil evidences at his disposal facilitate inferences and conclusions which contribute materially to the further successful exploitation of the area he has studied.

Petroleum is found in all the geological formations from the Silurian upwards, but economic deposits are restricted practically to the palaeozoic in North America and the Tertiaries of California and elsewhere. In Roumania the most important petroliferous deposits range up to the Pliocene series, the Oligocene, Eocene and Miocene having also proved to be productive in that country.

The types of rocks in which the oil is generally found are known as sedimentary or water formed rocks. They are accumulations formed in past ages, at the bottoms of seas and lakes, from material varying in composition and size of particle with the nature of the land which bordered those waters.

These rocks through various 'weathering' causes became disintegrated and decomposed and finally found their way to some place of rest at the sea or lake bottom.

Another factor in the formation of many sedimentary deposits is the appreciable amount of animal remains in the form of calcium carbonate. This substance derived from the hard parts of the animal inhabitants of past seas and lakes has practically alone

produced beds of great thickness, as witness the chalk and limestones.

It is clear that very many variations in quality can be expected in deposits which have been formed under diverse circumstances and from so many possible raw materials.

Petroliferous rocks or deposits are usually some form of sand, sandstone or limestone.

The old idea that oil existed in pools or lakes in the bowels of the earth no longer holds good and perhaps the familiar analogy of a brick saturated to overflowing with soda-water may give some impression of the state of oil and its accompanying natural gas in the sands or other rocks in which it is found. The oil and gas, however, are under great pressure.

It is not assumed that the oil is discovered always in the exact place in which it has originated, on the contrary, it is believed that in many cases it has migrated, through various causes, such as geological disturbances involving vast rock movements, when its lightness as compared with water would come into play, the action of gravity, capillarity and the accumulated pressure of the gas contained by the oil, gaining access to places of storage where it is prevented from further movement by a covering of impervious rock (e.g., clay), and is retained by virtue of hydrostatic equilibrium in the inverted vessel formed by the impervious cap. Such structures may be dome-shaped, as for example, at Spindle Top, or anticlinal, i.e., inverted V-shape or any number of modifications of these and other similar forms.

In his search for petroleum the prospector is guided, after general geological features have been ascertained or, during the course of his investigations on

these features, by indications such as the following:

In an oil country there are frequently visible signs that indicate the presence of petroleum in the neighbourhood. For instance, mud volcanoes, through which hydrocarbon gases force their way in bubbles to the surface, are found in the fields of Trinidad, Roumania and elsewhere. These gases are of the same nature as the natural gas which accompanies the crude oil exploited by wells and are derived undoubtedly from the same source.

Seepages or traces of oil that have arrived through fissures in the ground or from exposed oil-bearing rocks which outcrop to the surface, are found as thin streaks of oil following a stream or as iridescent films where they are spread over the surface of the water.

Deposits such as the pitch lake of Trinidad may similarly be regarded as evidence of the presence, at some period of the Earth's history, of petroleum.

#### (d) **Exploitation**

The earliest attempts at extracting petroleum from the earth appear to have been made by means of pits or crater-like holes in the ground.

In the primitive exploitation of this nature extraction was confined to those areas where the oil was readily accessible near the surface; operations were carried out in fact, on the outcrops of the oil-bearing rocks or in their close vicinity.

When this procedure became too slow through exhaustion of the few areas suitable for its application the early miners resorted to hand-dug wells.

The hand-dug well, which is to be seen in use to

this day in the Carpathian fields<sup>1</sup> and others, may be circular or square in section, the shape depending on the nature of the territory excavated. The circular wells are lined with a kind of basket work which is found sufficient to prevent the falling of débris on the miner below; the square section wells are dug in less stable ground, these are more strongly timbered, the timbers in this case forming a support to the sides of the well.

The depth of such shafts may be anything from 100 to 1000 feet but sometimes exceeds this figure and their diameter is usually a little over a yard.

The shaft is sunk until the oil is reached, the miners at the bottom of the hole working "solo" shifts.

The débris is removed by means of buckets raised and lowered from a winch placed at the top of the shaft.

Ventilation is effected by roughly constructed bellows which blow air through a form of stove pipe carried to the bottom of the hole and large reflecting mirrors are arranged to transmit light down the shaft.

The oil is drawn to the surface in wooden or leather buckets actuated from the winch either by horse or man-power and it is recorded in the Roumanian oil-fields that as much as 18-20 tons of oil per 24 hours have been extracted from hand-dug wells 500 feet in depth.

When the first oil source is exhausted further sinking is resorted to. During this operation a sudden influx of oil may surprise the miner and drown him before his partners on the surface can drag him up

<sup>1</sup> Masterson, "Petroleum Industry of Roumania," *J. Inst. Pet. Tech.* iv. 79.

and in order to obviate such a calamity information as to the nature of the strata below is obtained by probing the bottom of the shaft with a sounding-rod which is driven two or three yards in advance of the actual workings. Despite this and other precautions the life of the digger of hand-wells is hazardous at the best of times.

The introduction of modern plant and machinery for the exploitation of petroleum dates from 1858 when an American, Colonel Drake, in drilling for brine at Titusville, Pennsylvania, fortuitously struck oil.

From this time onwards the exploitation of petroleum became a recognised industry until it has acquired to-day a predominant position among the industries of vital importance.

After the usual preliminaries of levelling, etc., a derrick or rig constructed either of timber or steel is erected over the bore hole site. This structure facilitates the handling of the long "strings" of drilling rods, tools and casing which are manipulated from the crown of the derrick by means of block and tackle controlled from the ground.

Of the various systems of drilling in vogue each is more suitable under certain given conditions, thus the Canadian and Pennsylvanian percussive methods of drilling are more suited to the necessarily slow and careful drilling required on unproved territory, whereas either the water-flush percussion or the rotary method in known formations is the quickest method of reaching depth.

The percussive method of drilling is essentially one in which a hole is punched into the rocks by regularly delivered blows from a heavy bit supported from a walking-beam, from which a reciprocating motion is

transmitted by rope in the Pennsylvania rig, or iron poles in the Canadian (Galician modification)<sup>1</sup>.

In these systems when the rock is soft and cavey the sides of the bore hole must be supported by cylindrical wrought-iron or steel tubes, known as casing, as the hole proceeds in depth, otherwise difficulties of caving-in and accumulation of débris would prevent progress.

The water-flush rotary system employs normally in soft formations a fish-tail shaped bit which is rotated at the end of a substantial drill system through which mud-laden water circulates. This mud carries away with it the débris which would otherwise accumulate at the bottom of the hole and further serves to cement the walls of the well so that a very deep hole may be drilled before casing is necessary, this considerably facilitates rapid work since it reduced the delays occasioned by holding up drilling in order to put down the casing, and incidentally, the system is a great saver of casing.

Apart from the inconveniences that naturally arise in work which is being done at great distance from and out of sight of the operator, there are additional difficulties introduced by nature into the task of the oil-well driller in the form of intruding water.

The dangerous waters to be overcome in a well are those which in certain oilfields are situated above the impervious cap overlying the oil-bearing strata.

Should these waters be allowed to enter the oil-sand, the well is almost certainly lost as a producer. The enormous pressure of these superincumbent waters is enough frequently, to drive the oil completely away, the sands are then mere reservoirs of

<sup>1</sup> Ash rods were used originally.

water and the oil strata in the immediate vicinity is in danger of becoming water-logged.

A distinction must be drawn between circulating waters above the impervious beds and water which is frequently found locked up with the oil itself.

It may easily be imagined then, that in unproved territory where the water levels can be estimated, at the best, only approximately and where they may be numerous, the work to be accomplished in shutting-off the water is considerable, calling for the greatest patience and skill from the oilfield engineer.

On the successful completion of the well it is said to be "brought-in" as a producer. If the well is not a "gusher" ("spouter" or "fountain"), it has to be bailed or pumped.

In the case of the "gusher" or flowing well the greatest care has to be exercised in the initial stages, that the oil is all captured and that the losses due to evaporation and dispersions are reduced to a minimum. When the well begins to flow the oil is accompanied by enormous volumes of gas under huge pressure, which makes the control exceedingly laborious and risky. It is during this period that the danger of fire is greatest and every precaution is taken to prevent the access of gas to boiler sheds, etc. Once controlled, the gas is led away for use as fuel under the boilers or in gas engines, or if in sufficient quantity to gas-holders, and the oil is diverted into suitable containers for preliminary settling to rid it of sand and water previous to transmission by pipe line to the refineries.

After a period of flow, there follows a period of quiescence during which time the production falls—perhaps occasionally enlivened by intermittent flow—

and bailing is then resorted to. This means that cylindrical vessels with valves at their bases are lowered at the end of wire ropes into the well. They perform the double function, not only of raising their quota of oil but also when necessary, of clearing the accumulated mud from the bottom of the hole, thus allowing of more easy access of the oil from the surrounding neighbourhood. When the production falls to a fairly steady minimum, where bailing, which requires the attention of an individual workman, is uneconomical, it is usual to insert pumps in the wells. These pumps are actuated by a transmission system enabling a number of wells to be pumped simultaneously from a central power plant, thus reducing the cost of production to the lowest limits.

#### (e) Refining of Crude Oil

Petroleum being a mixture of hydrocarbons, it is possible, roughly, to separate its component parts by the difference of their boiling points, i.e., by fractional distillation.

The perfect isolation of any definite chemical compound is a difficult task in pure chemistry. The distillates obtained in practice, however, may be so arranged as to give products, having given densities, fixed limits of boiling point and fairly constant composition.

The distillation of crude oil in the refinery is carried on in stills of various patterns, a form generally adopted to-day consists of a horizontal boiler with dome, manhole and other fittings as shown in fig. 1. These stills have a capacity of 10,000–90,000 kilograms. An average length for such a still is 8 metres



and diameter 2·8 metres with a capacity of 40,000 kilograms.

The stills are set in a battery of four or more.

The battery of stills may be run either intermittently or continuously. The intermittent running consists in charging the stills and applying fire underneath until the distillation is complete and then withdrawing the fire, allowing the still and residues to cool.

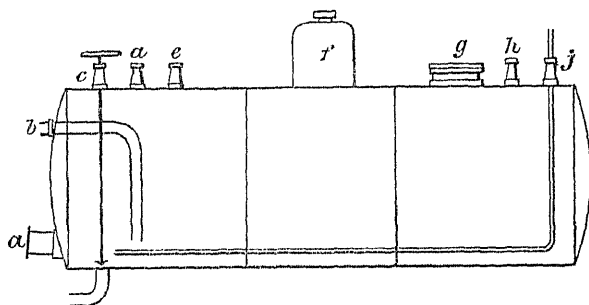


Fig. 1. Crude still.

In its simplest form, the unit in this plant is a still and a condenser. In this form, however, heat is lost from the cooling of the vapours during the period of condensation and heat is also lost from the residues which have to cool in the stills.

A more economical arrangement is where the pipes conducting the heated vapours to the condenser are made to pass through a forewarmer wherein they warm up the crude oil which subsequently passes to the next still requiring to be charged; and, the heat of the residues at the end of the distillation is not entirely wasted, for by means of another forewarmer, the pipes conducting the residues to their reservoir pass likewise through crude oil, thereby delivering up some of their heat in a useful manner.

From both these forewarmers (interchangers or preheaters, as they are alternatively called), benzine vapours are distilled off—the first and most volatile fractions of the crude—and are sent through condensers straight to the tailhouse, where the distillates are collected and distributed, and are run out as light benzine.

The arrangement of still and forewarmer is shown in purely diagrammatic form in fig. 2. The vertical forewarmer  $V$  is arranged to serve the whole

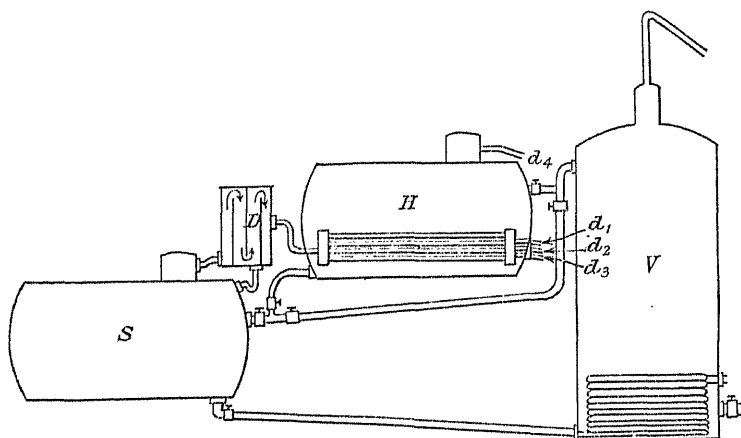


Fig. 2. Arrangement of forewarmers.

battery whereas the horizontal forewarmers  $H$  each serve a pair of stills  $S$ . The delivery pipes  $d_1$ ,  $d_2$ ,  $d_3$  come through the horizontal forewarmer from the still and pass subsequently to the condenser (not shown in the diagram).

$d_4$  and  $d_5$  are the delivery pipes from the horizontal and vertical forewarmers respectively and pass similarly to the condensers.

Between the still  $S$  and the delivery pipes which pass through the horizontal forewarmer  $H$  is installed

a scrubber or dephlegmator *D* the function of which is to clean or scrub the vapours as they pass from the still on their way to the condenser. This operation is effected by means of baffle-plates as shown in the figure. The heavier, more readily condensed fractions cool and liquefy on the plates instead of passing on with the lighter fractions, thus rendering a more even or homogeneous product.

The distribution of cocks for charging the stills is seen in fig. 3. By suitable arrangement of these cocks

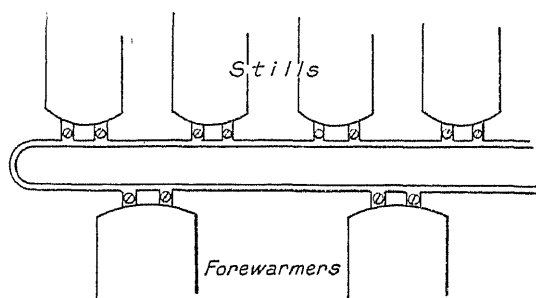


Fig. 3. Location of cocks.

it is possible to charge any particular still of the battery without disturbing the running of the others.

The course of a complete run is as follows:

The crude is charged in the still from the horizontal forewarmer, or, it may be convenient for the sake of speed when starting up, if, for example, the horizontal forewarmer be empty, to run direct from the vertical forewarmer.

The fire is put in when the still is about one third charged and the lighter fractions of benzine soon begin to distil over.

When these fractions arrive at the tailhouse the density is taken and they are directed into the par-

ticular division of the receiving box as is appropriate. The density test is made each hour and is recorded as a check on the speed of distillation.

The separation of the distillates coming over to their particular receiving tanks is effected by some device such as is shown in fig. 4, where, for example, *B* is the division for light benzine, *C* crude benzine, *D* kerosene distillate, *E* gas oil and *F* a compartment reserved for any products coming over during the first few minutes of a run, contaminated by the heavier

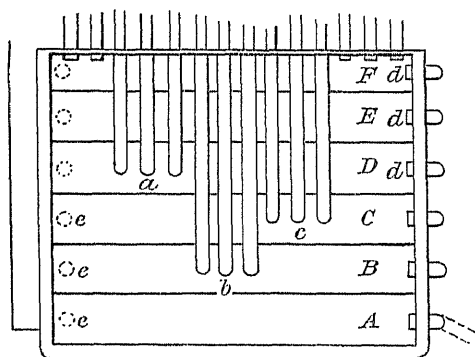


Fig. 4. Receiving box.

distillate left in the leads or serpentines of the condensers from the previous distillation. The products are run off from the top of each compartment and fall by gravity to the receiving tanks. A periodical check measurement is made of the quantity of distillate collected in these tanks and when they are full their contents are pumped to the rectifiers, agitators or the larger storage tanks as necessity arises.

At the receiving box (fig. 4) water can be run off from the bottom of each compartment; there is also an arrangement by which a heavy iron cover can be instantly let down on the receiving box in case of fire.

A certain amount of waste by evaporation is inevitable in this uncovered box and more modern de-

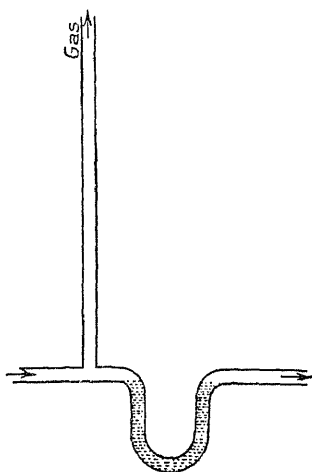


Fig. 5. Gas trap.

is placed in the delivery pipes immediately before the receiving box and outside the tailhouse. This is shown in fig. 5. This gas is led away to be burnt as fuel beneath the stills.

The limits of density between which the products are divided vary with the type of crude treated and the products desired. The densities may be for example:

|             |            |                |
|-------------|------------|----------------|
| Up to 0.705 | run off as | Light Benzine; |
| „ 0.790     | „ „        | Crude Benzine; |
| „ 0.863     | „ „        | Kerosene;      |
| „ 0.878     | „ „        | Gas Oil;       |

at which density the distillation is stopped, the residue in the still being fuel oil. When the density has attained 0.750–0.760 superheated steam is passed into the still to aid the distillation and is allowed to pass until the end.

The advantageous action of the steam is that by its

pressure in the still it drives the oil vapours out with it; vapours that otherwise might become changed in composition or "cracked" by prolonged contact with the heated walls of the still.

A cock is so placed in the steam delivery that any steam previously condensed to water can be blown out before opening into the still. The superheater is placed in close proximity to the stills. A temperature of about  $175^{\circ}\text{C}$ . is maintained.

The fire is extinguished at a little above the point of change into gas oil, i.e., about 0.863.

When the run is completed, an average time being about twenty-four hours, the residue is allowed to cool until a safe temperature is arrived at when it may be sent through the vertical forewarmer to the reservoirs, the time of cooling being about an hour and a half.

The benzine distilled off a very light crude oil by the use of forewarmers or preheaters as they are also called, amounts to 8-12 % in the horizontal and about 1 % in the vertical (calculated on the crude oil).

In the continuous running now in operation in most large refineries the first still of the battery is charged and fire applied until a certain temperature is attained, which temperature is kept constant for that still, and a certain density being reached the residue at that point is run by gravity into the next still (which is set on a lower level) where a higher temperature is maintained and a product of higher density obtained, and so on throughout the battery; each still having a temperature higher than that maintained at the preceding one.

In this manner no time is lost between the charges,

less combustible is necessary and less wear and tear is experienced by the stills, but the quality of the products is said to suffer.

As an example of the running of a continuous installation the following may be taken. The installation has one vertical and three horizontal forewarmers working with six stills.

*Example of continuous running:*

|   |        |
|---|--------|
| Vert. forewarmer gives distillate average density | 0.698; |
| Hor. „ No. 1 gives distillate average density     | 0.705; |
| „ „ No. 2 „ „ „                                   | 0.708; |
| „ „ No. 3 „ „ „                                   | 0.712; |
| Still No. 1 „ „ „                                 | 0.775; |

*giving a crude benzine of 0.755.*

|  |        |
|--|--------|
| Still No. 2 gives a distillate average density | 0.807; |
| „ No. 3 „ „ „                                  | 0.821; |
| „ No. 4 „ „ „                                  | 0.842; |

*giving a kerosene of 0.822 and flash point 31°–32° C.*

|  |        |
|--|--------|
| Still No. 5 gives a distillate average density | 0.863; |
| „ No. 6 „ „ „                                  | 0.882; |

*giving a gas oil of 0.872 and flash point 85° C. and leaving a residue (fuel oil) of 0.915–0.940.*

The condensers are rectangular iron tanks in which cold water circulates round the delivery pipes coming straight from the forewarmers.

An arrangement of condensers is shown in fig. 6, tanks 2, 3, 4 and 5 are for a battery of four stills. Tank 6 serves the horizontal forewarmers and tank 1 serves the vertical forewarmer and at the same time is used by one still (No. 1) which is not in the battery.

Fig. 7 shows a device by means of which compressed air is blown through the residue discharge pipe. In the summer months this is not necessary but in times

when congelation of a paraffinous distillate is a possibility it is desirable to keep the pipes free from such a

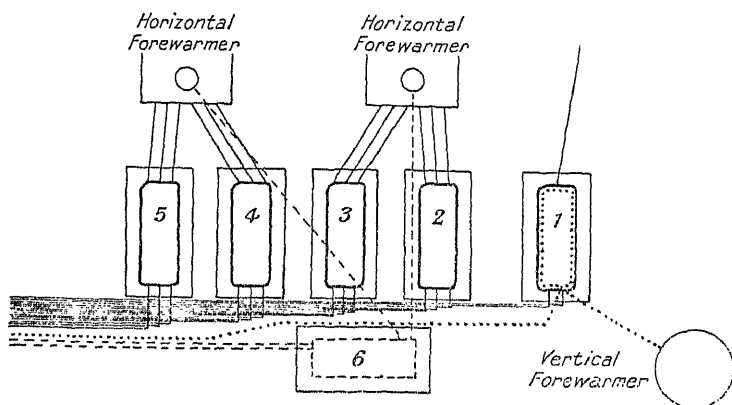


Fig. 6. Condensers.

deposit. The siphon tube *S* prevents the return of oil to the compressor should the cock *C* be defective.

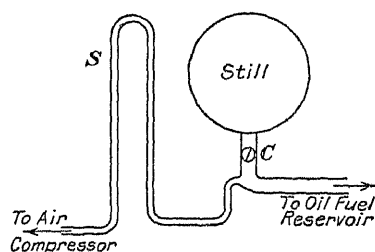


Fig. 7. Clearing device for still discharge.

**Fuel.** Oil fuel or natural gas are the usual combustibles. Oil is employed under both the steam boilers and the oil stills. The oil used is nearly always residue or fuel oil but gas oil is sometimes used either alone or mixed with the residue.

To effect complete combustion the oil is forced through an injector or atomiser. There are many



types of atomisers on the market, and many are of very simple design.

The atomiser shown in fig. 8 is a very simple and

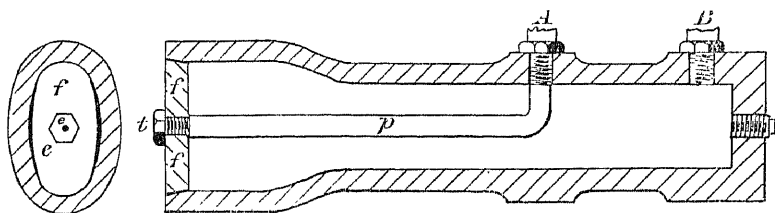


Fig. 8. Atomiser.

efficient piece of apparatus. Oil enters at *A* and steam at *B*, the steam has the effect of heating the oil on its journey through the passage *p*, escaping at *e* (in the end view). The plate *f* is cut slightly conically so that on tightening up the nut *t* the steam escape can be regulated. The total length is 12 cms.

Fig. 9 shows another type of atomiser, oil enters at

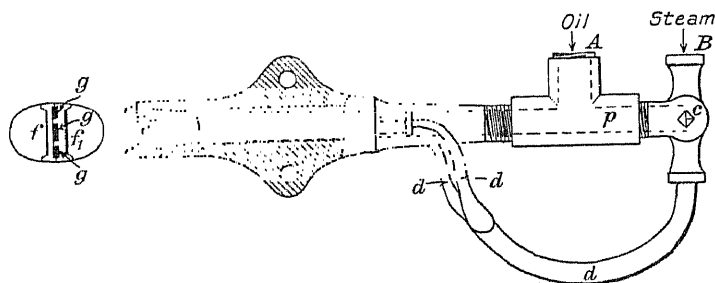


Fig. 9. Atomiser.

*A*, and steam at *B*. By arranging the three-way cock *C*, the steam is directed along the pipes *dd*, and meets the oil at *e*, or, it may also assist in the flow of the oil through the pipe *p*. The end view gives an idea of the distribution of steam and oil. Steam arrives at *f* and *f*<sub>1</sub> and oil or a mixture of oil and steam, as the

case may be, at *g*, the black spaces (in the end view) being the outlets of the atomiser.

A small serpentine through which steam circulates is fitted in the fuel reservoir in order to keep the oil less viscous which is of some importance in the winter months.

The quantity of combustible used in refineries is a question which has only of recent years received the attention that it deserves. In a very small refinery known to the present writer liquid fuel is burnt in open dishes very much like meat tins. In such archaic

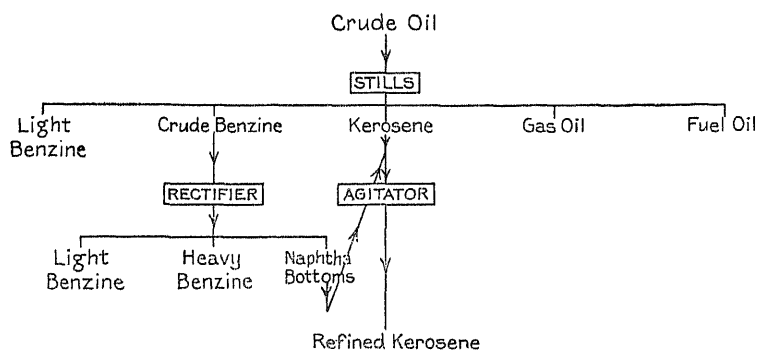


Fig. 10. Flow-sheet of simple refinery process.

concerns a large fuel consumption exists and is likely to continue until the small refineries realize that improvements are no longer luxuries but necessities. At the refinery mentioned above a fuel consumption of from 15–20 % (calculated on throughout of crude) is confessed to and probably the true figure is above this.

With the refinement of atomisers fuel consumption is reduced to from 6–10 % about one-third of which is used by the stills.

The flow-sheet shown in fig. 10 gives a simplified scheme of the refinery processes.

It must be understood, however, that this is only one simple scheme and that other methods prevail.

The control of the whole process of petroleum refining depends entirely on the nature of the crude oil passed through the refinery. For this reason and since the quality of oil delivered from the oilfields is liable to great variations it is impossible for the refiner to keep to a rigid programme and he must be ready to adjust his methods and plant to any circumstances that may arise.

Although no very definite line can be drawn between paraffinous and asphaltic crude oil it is possible roughly to divide crude oil under these two classes, recognising, nevertheless that paraffinous oils may contain asphaltic bodies and vice versa<sup>1</sup>. It is generally true that all types of oil are found in all fields and that any particular field said to produce a certain type of oil is so described because that type preponderates in the total production. Generally speaking, from the point of view of petrol yield, the paraffinous oil is more valuable.

TABLE II.

*Commercial products of crude Roumanian petroleum.*

|                   | Moreni |        | Baicoi |        | Razvad |        |
|-------------------|--------|--------|--------|--------|--------|--------|
| Density at 15° C. | 0.8085 |        | 0.8592 |        | 0.8859 |        |
|                   | %      | D 15   | %      | D 15   | %      | D 15   |
| Light benzine     | 35.38  | 0.7104 | 4.28   | 0.7178 | 10.52  | 0.7172 |
| Heavy benzine     | 9.29   | 0.7658 | 15.68  | 0.7581 | 5.29   | 0.7685 |
| Kerosene          | 14.99  | 0.8182 | 27.75  | 0.8200 | 14.47  | 0.8170 |
| Gas oil           | 8.17   | 0.8796 | 10.27  | 0.8840 | 11.46  | 0.8753 |
| Fuel oil          | 31.01  | 0.9542 | 41.07  | —      | 58.07  | 0.9574 |

<sup>1</sup> See Table XXX, Appendix.

The above figures show the approximate compositions in commercial products of three Roumanian crude oils.

After the crude oil distillation, a sketch of which has been given above, the further treatment of the distillates depends entirely on the nature of the products and the characteristics demanded for the finished article.

TABLE III.

*Typical products in crude oil refinery.*

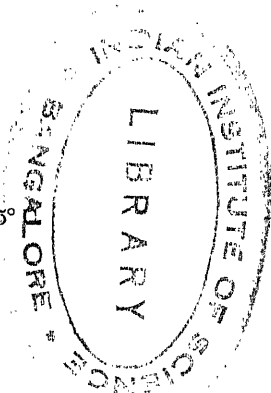
| <i>Light benzine.</i>          |   |              | <i>Heavy benzine.</i>       |   |              |
|--------------------------------|---|--------------|-----------------------------|---|--------------|
| Density 15° C. = 0.712.        |   |              | Density 15° C. = 0.770.     |   |              |
| Distillation: began 38°–45° C. |   |              | Distillation: began 75°–85° |   |              |
| At 60° distilled 8 %           |   |              | At 100° distilled 1 %       |   |              |
| 70°                            | „ | 21           | 110°                        | „ | 5            |
| 80°                            | „ | 40           | 120°                        | „ | 24           |
| 90°                            | „ | 57           | 130°                        | „ | 50           |
| 100°                           | „ | 73           | 140°                        | „ | 75           |
| 110°                           | „ | 84           | 150°                        | „ | 87           |
| 120°                           | „ | 90           | 160°                        | „ | 93           |
| 130°                           | „ | 94           | 170°                        | „ | 96 flask dry |
| 140°                           | „ | 97 flask dry | 175°                        | „ | 98.5         |
| 150°                           | „ | 98.5         | Residue                     |   | 0.9          |
| Residue                        |   | 0.7          | Loss                        |   | 0.6          |
| Loss                           |   | 0.8          |                             |   |              |
|                                |   | <u>100.0</u> |                             |   | <u>100.0</u> |

| <i>Refined kerosene.</i>            |   |              | <i>Gas oil.</i>                        |  |  |
|-------------------------------------|---|--------------|--|--|--|
| Density 15° C. = 0.8151.            |   |              | Density 15° C. = 0.868.                |  |  |
| Flash-point 32°·5 C. (Abel-Pensky). |   |              | Flash-point 89° C. (open).             |  |  |
| Colour 200 (Stammer).               |   |              | 70° C. (Pensky-Martens)                |  |  |
| Distillation: began 123°–145° C.    |   |              |  |  |  |
| At 150° distilled 1 %               |   |              | <i>Fuel oil.</i>                       |  |  |
| 200°                                | „ | 66           | Density 15° C. = 0.943.                |  |  |
| 250°                                | „ | 91           | Flash-point 141° C. (open).            |  |  |
| 280°                                | „ | 96.5         | 116° C. (Pensky-Martens).              |  |  |
| Residue                             |   | 2.3          | Distillation: began 219°–231° C.       |  |  |
| Loss                                |   | 1.2          | At 310° distilled 18.1 % being 0.8910. |  |  |
|                                     |   | <u>100.0</u> |  |  |  |

1306

665.5

N18



It may be that the residues are further distilled in so-called tar stills for the production of lubricating oils or a distillation of the residues under reduced pressure and in vacuum stills may be resorted to. Paraffin wax, pitch, coke or vaseline may be prepared, details of the manufacture of which are given in the works quoted in the bibliography.

Reverting then, to the raw distillates obtained from the first or crude-oil distillation. The general treatment is one of agitation with sulphuric acid followed by agitation with soda and washing with water.

Throughout these processes careful checks are made in the laboratory on the extent to which the chemical reactions have taken place and on the quality of the resultant oils.

The above specimen figures are submitted as typical of some of the products that may be found in the crude oil refinery.

## CHAPTER III

### PETROL

#### (a) Rectification

It has already been mentioned that the volatile fractions of light benzine collected from the forewarmers in the crude oil distillation are usually sent straight to the storage tanks; in the more restricted treatment and more moderate temperatures under which they have been produced there is less liability as compared with the benzine from the stills for contamination with high boiling-point bodies which it is the object of the rectifying to remove from the more volatile products.

The crude benzine from the stills, however, is definitely a mixture of substances with wide limits of boiling-point. The whole operation of rectification is to concentrate fractions from this mixture of hydrocarbons with given specific gravities, fixed limits of boiling-point and composition as nearly constant as it is possible commercially to obtain.

The process, then, is a repetition of the treatment of the crude oil, in so far as it is a fractional distillation, but there are additional precautions and more delicate handling.

The stills or rectifiers in which this re-distillation is carried out are heated by steam pipes.

Fig. 11 shows the horizontal pattern of the Heckmann still which is the most typical benzine rectifier.

In American practice these rectifiers are known as steam stills.

In the figure, *A* is the still heated by the steam pipes(*S*). By the action of this heat vapours are formed in the still; these rise through the column *B*, through the series of iron baffle plates *b* (fig. 12), and deposit as condensed products the less volatile fractions. As

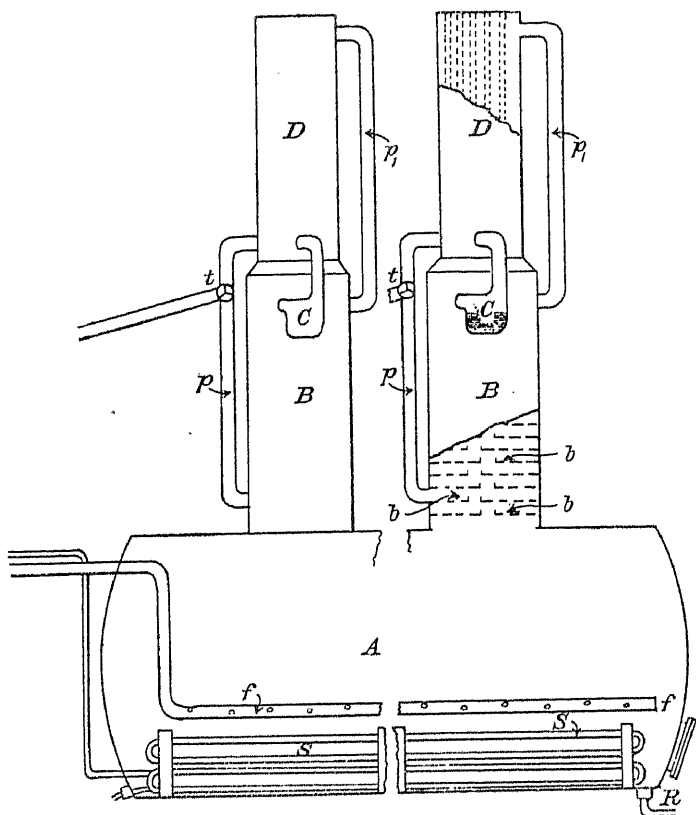


Fig. 11. Heckmann rectifier.

the vapours rise, then, they become richer in light parts, having left the heavier parts behind.

From the columns the pipes *p* conduct the vapours to the dephlegmator *D*, a cylinder with a number of vertical pipes through which cold water circulates.

Again, the less volatile fractions condense and flow back to the columns by means of the siphon *C*, which will allow of the passage of this liquid but not of the ascending or descending vapours on either side of it.

Passing down the dephlegmator the vapours are finally conducted to the condenser (not shown in the figure).

The condensed benzine passes through an inspection box of special construction shown in fig. 13, where *A* is the delivery pipe from the condenser: the benzine rises in the column *C*, until it overflows through the holes indicated into *B*, from whence to the receiving tanks and finally to the reservoirs.

From the level of liquid in the column *C*, the rate of flow can be estimated and the steam heating accordingly regulated, here also the temperature of the benzine can be taken.

The density is taken and recorded every hour and the cut-out point between light and heavy benzine thereby decided.

When the density of the products reaches about 0.750, direct steam may be given (through the perforated distributing pipe *f*, fig. 11) but with some crude benzines this is unnecessary.

With the use of direct steam an amount of water

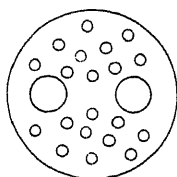
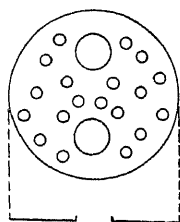


Fig. 12. Baffle plates.

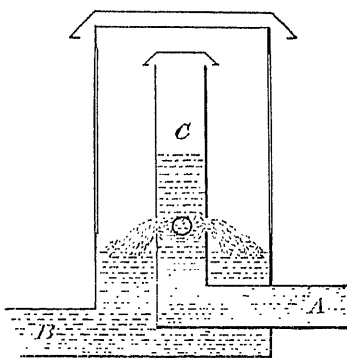


Fig. 13. Inspection box.



distils over and is run off from a siphon arrangement which is connected to the pipe *A* of the inspection box shown in fig. 13.

The object of rectification as stated above is to obtain a product as homogeneous as possible. It is necessary with this end in view to run a rectifier with no sudden changes of temperature.

In the still this state of affairs is more or less assured by the system of distilling with steam pipes but in the condensing columns there is a liability for the water to become over-heated. This will allow a product with a higher boiling point to pass the inspection box. A sudden cooling of the columns by an irregular supply of cold water to the condenser column will then allow only lighter fractions; the result being an inferior product of fractions with boiling points within wide limits.

If the quality of the product can be sacrificed to an increased output the crude benzine may readily be distilled without the use of the columns and dephlegmator, this being effected by the adjustment of a three-way cock (*t* in fig. 11) so that the vapours ascending pass through the pipe *p* and straight on to the condensers.

The residue at the end of the rectification (called usually "naphtha bottoms") is run off at *R*, cooled in a small condenser or cooler and run down into a tank from which it is subsequently drawn to be mixed with the kerosene distillate as is shown in the flow-sheet on page 27.

The addition of the naphtha bottoms reduces the flash-point and density of the kerosene and it is often difficult to refine, so that it must be added with due regard to these points.

A usual running of the rectifier is to about 0.750 for light benzine after which density the products are made to run to the heavy benzine receiving tank until a density of about 0.770 is attained at which point steam is cut off and the 'bottoms' run down to their tank.

The quantities of light and heavy benzine vary with the quality of crude passing through the refinery.

Figures are here given of rectifications carried out on crude benzine derived from Roumanian crude oil.

TABLE IV.

*Samples from Heckmann rectifier.*

| <i>Sample I</i>                |        | <i>Sample II</i>               |        |
|--------------------------------|--------|--------------------------------|--------|
| Benzine D <sub>15</sub> 0.705. |        | Benzine D <sub>15</sub> 0.720. |        |
| Distillation began at 58° C.   |        | Distillation began at 63° C.   |        |
| - 70° C.                       | 7 ccs. | - 80° C.                       | 3 ccs. |
| - 80°                          | 30     | - 90°                          | 22.5   |
| - 90°                          | 59     | -100°                          | 66.5   |
| -100°                          | 83     | -110°                          | 95     |
| -110°                          | 98.5   | -114°                          | 99.5   |
| Residue and loss               | 1.5    | Residue and loss               | 0.5    |
| <i>Sample III</i>              |        | <i>Sample IV</i>               |        |
| Benzine D <sub>15</sub> 0.740. |        | Benzine D <sub>15</sub> 0.745. |        |
| Distillation began at 65° C.   |        | Distillation began at 78° C.   |        |
| - 90° C.                       | 8 ccs. | -100° C.                       | 2 ccs. |
| -100°                          | 66.5   | -110°                          | 41     |
| -110°                          | 90     | -120°                          | 83     |
| -120°                          | 98     | -130°                          | 97     |
| -130°                          | 99     | -140°                          | 98.5   |
| Residue and loss               | 1      | Residue and loss               | 1.5    |

The four laboratory distillations (Engler method) here recorded were made on products from a Heckmann rectifier which was working under test conditions.

The figures will be more readily appreciated, perhaps,

after a consideration of the method and meaning of the laboratory tests described in the chapter on examination and testing.

It may be pointed out, however, that these results serve to show what types of freak products may be obtained by careful control and manipulation of the rectifying plant.

The quality of the products made commercially is governed solely by the specifications on which are based the contracts fulfilled by the refineries.

For example, one purchaser buys a benzine on a distillation basis whereas another buys entirely on a density specification. In the first case the rectification of the benzine is a matter of paramount importance, whereas in the second case, so long as the density is not above, say, 0.720, the benzine may have come straight from the crude oil distillation and never have passed through the rectifier.

In the preparation of the very light and highly volatile products such as those used as anaesthetics, special cooling is arranged for in the condensers, for example, the provision of iced water.

### (b) Refining

The refining or deodorizing of petrol or benzine is effected by washing with sulphuric acid and caustic soda. This washing is carried on in an agitator or oil-washer which takes the form of a cylindrical vessel of iron with a conical bottom as shown in fig. 14. This shape allows of readily running off from the bottom the heavier acid and soda sludges, formed during the refining process, without undue waste of oil. The agitator is lined with sheet lead to protect the plates from being corroded by the action of the acid.

A percentage varying from 0·5–1 of sulphuric acid (sp. gr. 1·85) is given in two doses and mechanical agitation is effected, a wash with water ends the acid treatment. Agitation with soda then follows (the caustic soda being of 10–11° Baumé), and a final wash with water completes the process. The following

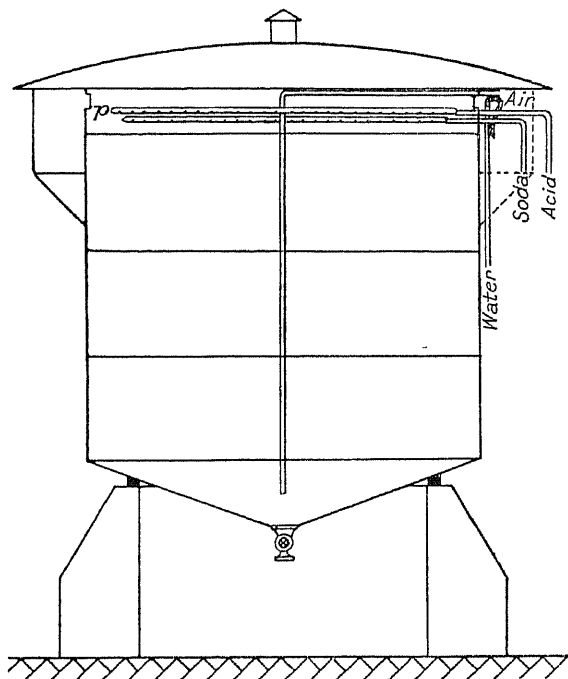


Fig. 14. Oil washer or agitator.

tabulated remarks show more clearly the procedure adopted.

1. Any water that may have collected in the bottom of the agitator is run off. The presence of water would interfere with the action of the acid and, furthermore, is a danger in the winter when it may freeze in the valves.

2. Agitation for one hour with 'dead' acid (that is, acid employed in the later washes of previous runs). The agitation must be fairly gentle as compared with kerosene refining in order to avoid undue loss from evaporation. The agitation may be effected by a gentle stream of compressed air as is the case in kerosene refining, or far better, in the case of benzine by means of a mechanical stirrer.

3. The acid sludge is allowed to gather to the bottom of the agitator for about one hour after the agitation has ceased and it is then run off.

4. Agitation with fresh acid for one hour, deposit an hour and sludge run off.

5. Wash with water, gentle agitation, one hour deposit and run off.

6. Agitation with soda for ten minutes; half an hour deposit and run off.

7. Wash with water for half an hour deposit and water run off. The process is then complete and the benzine is pumped either to storage or straight to tank cars for transport.

The sulphuric acid employed is run from its reservoir into a small tank the cover of which fits well and is air-tight, compressed air is then turned on to drive the liquid up into the agitator; the acid being delivered therein by the pipe *p*, in fig. 14, which is perforated in a manner to distribute the acid over the surface of the oil.

The same method is used with the soda which has a separate tank in which the solid caustic soda is previously dissolved by steam. The soda is distributed by a circular pipe running parallel to *p*.

Refining in the summer months is, when convenient, relegated to the darkness and coolness of the

night, for the midday heat during the acid reactions is not conducive to good results and in any case the losses during agitation are greater in the hot midday air.

The quantity of reagents used varies with the quality of the oil to be refined but the following table indicates within what normal limits the figures lie. Figures for kerosene are given for comparison.

TABLE V.  
*Quantities of reagents employed.*

|          | H <sub>2</sub> SO <sub>4</sub> | NaOH     |
|----------|--------------------------------|----------|
| Benzine  | .5 -1 %                        | .05-1 %  |
| Kerosene | 1.25-2 %                       | .15-35 % |

These percentages are on the weight of oil treated.

It may here be mentioned that an alternative method of benzine refining has been suggested where the benzine in place of being agitated is caused to percolate through columns of acid and soda respectively thus saving the wastage caused by agitation and consequent evaporation in a washer. Contact with the reagents, it is stated, is sufficiently intimate to render a well-refined product.

The method is described thus: the distillate flows through vessels containing respectively, sulphuric acid, caustic soda, washing water and finally, a filtering mixture of sawdust and salt. The first three vessels contain the acid. The vessels are all closed and half filled with the reagent, and are arranged at successively lower levels. The spirit is run into the first vessel through a perforated tube passing to the bottom of the vessel, it rises through the acid and

escapes through a tube at the top of the vessel to the bottom of the next and so on.

The object of the chemical treatment in refining is to remove those bodies that give the petrol an evil smell; this smell would render the oil useless for cleaning purposes and unpleasant in use as fuel. Similarly, the substances removed in the refining process are those that would favour the tendency to 'gum' and foul the cylinders of the internal-combustion motor in which the oil is used.

The substances that impart a bad smell and occasionally a bad colour to the crude benzine are tarry, resinous or asphaltic bodies, certain unsaturated hydrocarbons and bodies containing oxygen.

The chemical reactions taking place between the oil and the acid are but little understood.

On the one hand it is maintained that the products formed during the process of distillation are oxidised, become soluble in the acid, and are thus eliminated from the oil mass. On the other hand the view is held that the treatment is dependent for its efficiency on the mechanical deposition or precipitation by the acid of the tarry substances which are held in colloidal solution in the oil; these bring down with them in their precipitation other deleterious ingredients of the oil.

The soda treatment removes any acids naturally occurring in the oil and further neutralises those formed by the action of the acid on the oil or traces of the sulphuric acid held in suspension throughout the oil mass.

Many substitutes for the reagents have been suggested but none has proved so successful in practice as the sulphuric acid and caustic soda.

## CHAPTER IV

### PETROL: OTHER SOURCES

#### (a) Casing-Head Gasoline

CASING-HEAD gas<sup>1</sup>, that is natural gas obtained from the oil or gas well when conducted through any length of pipe line, is found to condense and leave in the line a volatile liquid similar in nearly all respects to the lightest fractions from the distillation of crude oil. In most oilfield gas-lines of any size there are installed suitable traps to collect this liquid, thus preventing an interference with the free flow of gas.

Of recent years with the increased demand for petrol the recovery of this liquid has become a matter of considerable industrial importance.

In America, where it is known as casing-head gasoline, the production in 1914 reached some 43,000,000 gallons and in 1915 the yield from this source represented about 10 % of the total American gasoline production.

The constituents of natural gas are mainly gaseous paraffin hydrocarbons of which methane is predominant. Impurities in the form of carbon dioxide, water vapour and traces of nitrogen are also present. The relative proportions of these ingredients vary between very wide limits.

The following table shows analytical figures for a number of natural gases from various fields.

<sup>1</sup> See Allen and Burrell, "Liquefied products from natural gas, their properties and uses," *U.S. Bureau of Mines Tech. Paper*, No. 10. Burrell and Jones, "Methods of testing natural gas for gasoline content," *U.S. Bureau of Mines Tech. Paper*, No. 87.



TABLE VI.  
*Analyses of Natural Gases from various fields (Bacon and Hamor).*

|   | Constituents |                              |                             |               |             |                    | Remarks | Analyst            |   |  |
|---|--------------|------------------------------|-----------------------------|---------------|-------------|--------------------|---------|--------------------|---|--|
|   | Me-<br>thane | Car-<br>bon<br>mon-<br>oxide | Car-<br>bon<br>di-<br>oxide | Nitro-<br>gen | Oxy-<br>gen | Hy-<br>dro-<br>gen |         |                    | Other<br>hydro-<br>car-<br>bons                           | Other<br>consti-<br>tuents               |
| California—Fresno County,<br>Coalinga Field | 88.00        | ...                          | 11.10                       | 0.90          | ...         | ...                | ...     | ...                | Collected by G. H. Salisbury,<br>June 10, 1910            | G. A. Burrell                            |
| King's County, Sunset Field                 | 87.70        | ...                          | 10.50                       | 1.80          | ...         | ...                | ...     | ...                | Collected by I. C. Allen,<br>July 16, 1909                | G. A. Burrell                            |
| Los Angeles County, West<br>Los Angeles     | 91.00        | ...                          | 1.00                        | 5.20          | 0.10        | ...                | 2.70    | ...                | Collected by I. C. Allen,<br>July 23, 1909                | G. A. Burrell                            |
| Santa Barbara Co., Santa<br>Maria Field     | 62.70        | ...                          | 15.50                       | 1.40          | 0.20        | ...                | 20.20   | ...                | Collected by I. C. Allen,<br>August 5, 1909               | G. A. Burrell                            |
| Kansas—Allen County, Iola                   | 94.50        | ...                          | ...                         | 5.08          | 0.23        | ...                | ...     | H-trace<br>He-0.18 | Collected June 10, 1906                                   | Hamilton P. Cady &<br>David F. McFarland |
| Chase County, Elondale                      | 78.60        | ...                          | 0.15                        | 12.13         | 0.30        | ...                | 8.26    | He-0.56            | Depth 152', pressure 45 lbs.,<br>collected August 8, 1906 | Hamilton P. Cady &<br>David F. McFarland |
| Louisiana—Caddo Field                       | 95.00        | ...                          | 2.34                        | 2.56          | ...         | ...                | ...     | 0.01               | ...   | David F. McFarland                       |
| New York—Chautauqua<br>Cov, Fredonia        | 90.05        | ...                          | 0.41                        | 9.34          | Tr          | ...                | ...     | ...                | ...   | F. C. Phillips                           |
| Pennsylvania—McKean<br>County, Kane         | 90.38        | ...                          | 0.21                        | 9.41          | Tr          | ...                | ...     | ...                | ...   | F. C. Phillips                           |
| Washington County, Hous-<br>ton             | 84.26        | ...                          | 0.44                        | 15.30         | Tr          | ...                | ...     | ...                | Contains also trace of am-<br>monia                       | F. C. Phillips                           |

|                                       | 97-70 | ...  | 0-28  | 2-02  | Tr   | ...  | ...   | Specific gravity (air = 1)<br>0.5667 | ... | F. C. Phillips<br>C. C. Howard |
|---------------------------------------|-------|------|-------|-------|------|------|-------|--------------------------------------|-----|--------------------------------|
| Westmorland Coy, Murrysville          | 81-60 | 0-40 | 0-10  | 3-21  | 0-20 | 0-20 | 14-29 | ...                                  | ... | C. C. Howard                   |
| West Virginia—Marion County, Fairmont | 97-10 | ...  | 1-30  | 1-00  | 0-60 | ...  | ...   | ...                                  | ... | ...                            |
| Austria—Wels.                         | 91-50 | ...  | 0-30  | 4-60  | 1-50 | ...  | 2-10  | ...                                  | ... | ...                            |
| German—Neuengamme near Hamburg        | 92-05 | ...  | 0-65  | 7-30  | ...  | ...  | ...   | ...                                  | ... | ...                            |
| Hungary                               | 53-35 | ...  | 1-17  | 40-86 | 4-22 | ...  | 0-40  | ...                                  | ... | ...                            |
| Russia—Samara                         | 65-84 | ...  | 12-82 | ...   | ...  | ...  | ...   | Ethane 19-92                         | ... | ...                            |
| Daghstson                             | 77-30 | 3-50 | 3-60  | 8-90  | 1-80 | ...  | ...   | Olefines 4-80                        | ... | ...                            |
| Tchelcken                             | 93-07 | ...  | 2-18  | 0-49  | ...  | ...  | ...   | Olefines 3-26                        | ... | ...                            |
| Caspian Region                        | 92-89 | ...  | 0-93  | 2-13  | ...  | 0-98 | ...   | Olefines 4-11                        | ... | ...                            |
| Baku (Peninsula of Apsheron)          | 99-60 | ...  | 0-30  | 0-10  | ...  | 0-34 | ...   | ...                                  | ... | ...                            |
| England—Staffordshire, Charnmont      | 93-16 | 1-00 | ...   | 2-90  | ...  | ...  | ...   | Ethane 2-94                          | ... | ...                            |
| Sussex, Heathfield                    |       |      |       |       |      |      |       |                                      |     |                                |

See Burrell and Oberfell, "Composition of the natural gas used in 25 cities, etc.," *U.S. Bureau of Mines Tech. Paper*, No. 109.

The methods employed in the preparation of casing-head gasoline commercially depend generally on refrigeration and compression, the extents of application of which are controlled by the quality of the gas dealt with.

A pressure of about 300 lbs and cooling with water at ordinary temperatures are employed in some cases and in others refrigeration with only slight pressure.

Another method of extraction is to bubble the gas through a heavy oil which will take into solution the gasoline dissolved in the gas; the oil is then distilled and the gasoline collected as the first distillate.

The condensates obtained in these processes vary in specific gravity from 0.635 to 0.670; they consist chiefly of pentane, hexane and butane in solution and are practically identical with the 'straight-run' refinery products of the same range of boiling points.

The gasoline recovered is too volatile for the ordinary purposes to which that substance is put and in its raw state is exceedingly dangerous to handle; it is therefore blended with the heavier benzine from the crude oil distillation to produce a light benzine or petrol with the desired proportion of volatile constituents that render the blended products suitable for purposes to which the heavy benzine could not alone be put.

From the above it will be seen that a petrol so blended may be distinguished on analysis from the ordinary 'straight-run' light benzine, if the blending is done with no intent to conceal the process, by the unusually high percentage of low boiling point fractions round about 60° C. and a similar concentration of distillate near the higher boiling point.

The industrial recovery of casing-head gasoline has

been greatly stimulated as a result of the increased demand for light fuel for internal-combustion engines and it would appear that this industry will assume increasing importance.

Obviously with the greater proportion of highly volatile fractions the percentage loss by evaporation is greater with this type of spirit than with the straight-run product.

Although this must be regarded as a slight disadvantage from the point of view of economical use it bears with it the compensating factor that the particularly light fractions facilitate the starting-up of engines in which the spirit is used as fuel.

### (b) Cracked Spirit

It has been shown in the remarks on the distillation of crude oil that as the distillation proceeds so the products possess increasingly higher specific gravities and higher boiling points and it is generally assumed that the distillates have with slight exception the same chemical composition, as such, as they had when in solution in the original crude petroleum. In fact the process is one of fractional distillation. The products are known technically as "straight-run" distillates.

If, however, the heat is excessive and steam is not employed to carry the vapours off, decomposition products arise as the result of the contact of the vapours with the hot walls of the still. The reactions result in the destruction of some of the higher boiling-point products with the formation of products of lower boiling-points and lower specific gravities. The process is now one in which the products possess chemical structures different from those of the original constituents.

Various methods have been devised with the express intention of encouraging this decomposition in order to obtain an increased yield of the more volatile portions of the crude oil. The reactions are complex and not fully explicable in the light of our present knowledge but the application of the process on an industrial scale is of increasing importance<sup>1</sup>.

Originally worked for the preparation of permanent gas the treatment has been extended to the manufacture of kerosene, aromatic hydrocarbons such as benzene, toluene, etc., and petrol.

In most of the cracking processes conditions of high pressure as well as high temperature prevail so that questions of safe running and wear and tear of plant assume important roles.

The quality of the products obtained varies with the nature of the process employed. In some cases resinous bodies are produced which are soluble in the 'cracked' spirit. These bodies render the spirit unfit for the use as motor fuel and have given 'cracked' spirits generally a bad reputation.

Efforts have, of course, been made to eliminate from the finished product these and other undesirable ingredients and judging by the absence of complaints against the vast quantities of cracked spirits and blends of 'cracked' with straight-run spirits that have been on the market recently it must be admitted that in some of the processes industrially employed the initial difficulties have been overcome.

<sup>1</sup> See particularly Lomax, Dunstan and Thole, "The Pyrogenesis of Hydrocarbons," *J. Inst. Pet. Tech.* III. 36 (1916), to which an excellent bibliography is appended. Also Hall, "The cracking of oils, etc.," *J. Inst. Pet. Tech.* I. 147 (1914). Lewes, "The Chemistry of the cracking of Heavy Oils," *J. Inst. Pet. Tech.* I. 167 (1914).

The bad smell of cracked spirits which, it is thought, is often an exaggerated objection, is attributed to small quantities of sulphur and nitrogen compounds. It is possible, however, to free cracked spirits of these odours by chemical treatment with cupric oxide or sodium.

Cracked spirits have a higher content of unsaturated hydrocarbons than the straight-run refinery benzene.

The specific gravity of cracked spirit on the market averages 0.737; this, for the same distillation range, is somewhat higher than that of the normal product.

It should be understood that the cracking processes have only recently emerged from the experimental stage and that they are likely to attract a great deal of attention in the future.

Further remarks on the quality of cracked spirits will be found in chapter vi dealing with the uses of petrol.

### (c) Shale Naphtha

Although not truly petroleum spirit a small proportion of low boiling-point products comparable with petrol is recovered from the crude oil which is obtained from oil shale.

Oil shales<sup>1</sup> are dark brown to black in colour, they have a horny fracture and a specific gravity of about 1.75. They are to be distinguished from *oil-bearing shales* which latter, in their interstices, contain petroleum. The oil shales, however, contain a bitumenous substance, *kerogen*, which yields a tar or crude shale-oil when the oil shale is treated in the retorts. The extraction of oil shale from the earth is a systematic

<sup>1</sup> See Conacher, "Oil Shales and Torbanites," *Trans. Glas. Geol. Soc.* xvi. 164.

mining operation which is practised in Scotland, France and elsewhere. The products from the shale-oil industry of Scotland have had to compete with the petroleum distillates on the market, which latter compared oil with oil cost very much less to produce. The life of the shale oil industry has nevertheless been preserved from its infancy by the fortunate nitrogen content of the shale; this, on treatment yields ammonium sulphate which is of value as an artificial manure.

Furthermore, a happy stroke of nature has frequently arranged the proportion of nitrogen to vary inversely with the oil content so that the shales poor in oil are rich in ammonia thus enabling many tons of shale to be worked that would have to be abandoned if the oil content only were recoverable.

The products from the retorting of oil shale are as follows:

1. Permanent gas.
2. Naphtha.
3. Crude oil.
4. Ammonia water.
5. Spent shale.

The gas is burned as fuel under the stills, effecting an economy of fuel. Naphtha is collected from the condensation of the gases liberated during retorting. The crude oil is refined and distilled rendering a further quota of naphtha. The ammonia water is treated with sulphuric acid from the acid sludges, which remain after refining the oils, to produce sulphate of ammonia.

The percentage of mineral matter in oil shale is usually between 73–80 % and the commercial yield in crude oil is on the average 20 gallons per ton, rarely

exceeding 30 gallons per ton, the sulphate of ammonia working out at 44 lbs per ton.

The crude oil has a specific gravity of 0.860 to 0.890 and is much richer in the higher paraffins (which are extracted as paraffin waxes) than the average petroleum from oil wells.

Furthermore the crude shale-oil contains a higher proportion of olefines, naphthenes and benzenes.

In the retorting of the oil shales and distillation of the resultant products steam is introduced into the retorts and stills with the object of avoiding the decomposition of the paraffin hydrocarbons present.

The crude shale-oil is divided by distillation into naphtha and "once-run" oil. This is the second point at which naphtha is recovered; the first being from the condensed gases mentioned above.

The "once-run" oil is then treated with acid and caustic soda in a manner somewhat similar to that described under the refining of petrol though the treatment of shale-oils is more complicated than that of the corresponding petroleum products.

The oil (once-run) is again distilled producing naphtha (third and last point of recovery) burning oil, heavy oil, coke and paraffin-wax after the respective treatments necessary for the finished articles.

The yield in various products is given thus:

|                |     |     |      |
|----------------|-----|-----|------|
| Naphtha        | ... | ... | 6 %  |
| Burning oil    | ... | ... | 32 „ |
| Heavy oil      | ... | ... | 24 „ |
| Paraffin scale | ... | ... | 12 „ |
| Loss           | ... | ... | 26 „ |

The three naphthas are now treated together with acid and soda, using 0.1–0.2 % sulphuric acid in the first acid wash followed by 0.5 % acid, and 1 %



caustic soda (specific gravity of  $10^{\circ}$  Twaddell); they are then ready for the market.

The composition of shale naphtha is given as 60–70 % olefines and the rest chiefly paraffin hydrocarbons.

The high content in unsaturated hydrocarbons is reflected in the iodine value.

At this point, therefore, it is of interest to note the recorded iodine value limits of three typical spirits.

|  |        |
|--|--------|
| Refined American (containing products of cracking) | 20–25  |
| Shale naphtha ... ..                               | 75–100 |
| Normal petrol (straight-run petroleum spirit) ...  | 0–7    |

The light marketable products obtainable from oil shales have been graded in the past under the following specific gravities 0.680, 0.718 and heavier up to 0.750.

The total production of light distillates under the heading of naphtha from the Scottish oil industry amounts to some 5,000,000 gallons annually.

Shale spirit is often spoken of as “green naphtha” and is used principally as a solvent and motor spirit.

A typical shale motor-spirit gave the following results under test:

D 15. 0.7190.

*Engler distillation of 100 ccs.*

Initial boiling point  $40^{\circ}$  C.– $50^{\circ}$  C.

|                           |                |
|---------------------------|----------------|
| At $60^{\circ}$ C. ... .. | 0.5 %          |
| 70 ... ..                 | 4              |
| 80 ... ..                 | 25             |
| 90 ... ..                 | 45             |
| 100 ... ..                | 63             |
| 110 ... ..                | 75             |
| 120 ... ..                | 84             |
| 130 ... ..                | 89             |
| 140 ... ..                | 93             |
| 150 ... ..                | 95             |
| 167 ... ..                | 98             |
| Residue ... ..            | .6             |
| Loss ... ..               | 1.4            |
|                           | <u>100.0 %</u> |

## CHAPTER V

### EXAMINATION AND TESTING

#### A. ROUTINE TESTING

##### (a) Introductory

THE application of scientific methods in the industries is admittedly receiving an enormous impetus at the present time, and, in particular, the paramount importance of efficient testing of products has been made evident.

But before material progress can be made a systematic standardisation of testing methods is necessary—a standardisation in keeping with the scientific work of to-day.

We must define our terms, and adopt where necessary, our conventions.

It is indeed regrettable that the work of the International Petroleum Congress of 1907, 1909 and 1910 has had so small an effect in this country in the direction of helping us to choose standardised methods of testing petroleum products. It is to be expected that this matter will receive the attention at an appropriate time, of the Institution of Petroleum Technologists.

In order to obviate the unnecessary repetition that would be involved by treating properties and investigation of those properties under separate headings they are here dealt with together.

The testing of petroleum products is a means of

controlling the processes operated by the refiner; it is also a means of assuring to the buyer of those products that they conform to the specification to which his purchase has been made. Several of the actual tests performed are the same for both objects stated but the points of view and application naturally differ as the test is applied by manufacturer or purchaser.

The examination of a petrol from an unknown source may be undertaken in a systematic manner in order to discover, from an academic point of view, as much as possible of the nature of its composition and properties or, simply by means of routine tests, which will show rapidly whether the spirit is suitable for any particular purpose for which it may be required.

#### (b) Chemical

The chemical composition of petrol, like that of its parent crude petroleum, is difficult of determination. From the refined product the following classes of hydrocarbons have been isolated: paraffins, iso-paraffins, cyclo-paraffins and aromatic hydrocarbons.

The composition of any particular petrol is a problem in itself, depending as it does on the origin of the crude from which it has been produced, and also on the subsequent treatment it has undergone.

The four classes of hydrocarbons mentioned above comprise many individual members which have been isolated. Of these the most familiar are shown in the table on pages 54 and 55.

In the technical examination of petrol it is at present unnecessary to determine its precise chemical composition.

Nevertheless, as the methods of technical analysis

of petroleum products develop it is certain that more attention will be given to the question of chemical composition, the disclosure of which, after all, is the ultimate guide to the nature of the petrol or other product analysed. Methods will be devised by means of which an estimation of the chemical composition of a petroleum spirit will be within the limits of a routine test.

At the same time selective or synthetic processes will probably be sought to separate or obtain those compounds in petroleum spirits which, in the future, may be regarded as more valuable products for specific purposes, than the mixtures of various compounds of which the present marketed spirits are composed.

Petroleum spirits from American sources are composed very largely of paraffin hydrocarbons. Roumanian and Sumatra spirits contain aromatics to a greater extent than most others and Borneo and Caucasian spirits are characterised by a preponderance of hydroaromatic bodies.

For the purposes of calculation it may be taken that the elementary composition, that is the proportion of carbon and hydrogen present, is usually

84–85 % carbon,

15–16 % hydrogen.

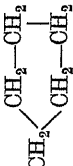

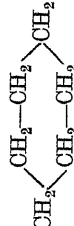



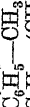

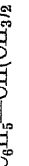
Heptane  $C_7H_{16}$  is composed exactly of 84 % carbon and 16 % hydrogen so that, from the point of view of elementary composition, normal petrol may be said to approximate most nearly to the paraffin hydrocarbon heptane.

The following tests are of use technically in the estimation of the value of a petrol.

1. Specific gravity.
2. Fractional distillation.

TABLE VII  
*Hydrocarbons in petrol.*

| Name   | Empirical formula | Structural formula            | B.P.      | Density              |
|--|-------------------|-------------------------------|-----------|----------------------|
| <i>Paraffin hydrocarbons</i> ( $C_nH_{2n+2}$ ) |                   |                               |           |                      |
| Normal pentane ...                             | $C_5H_{12}$       | $CH_3-(CH_2)_3-CH_3$          | 38° C.    | $D_4^{20}$ 0.6154    |
| Iso pentane ...                                | $C_5H_{12}$       | $CH_3-CH_2-CH(CH_3)-CH_3$     | 28° C.    | $D_4^{20}$ 0.6393    |
| Normal hexane ...                              | $C_6H_{14}$       | $CH_3-(CH_2)_4-CH_3$          | 69° C.    | $D_4^{20}$ 0.6770    |
| Iso hexane ...                                 | $C_6H_{14}$       | $CH_3-(CH_2)_2-CH(CH_3)-CH_3$ | 61° C.    | $D_4^{20}$ 0.6728    |
| Normal heptane ...                             | $C_7H_{16}$       | $CH_3-(CH_2)_5-CH_3$          | 98°·5 C.  | $D_4^{20}$ 0.7005    |
| Iso heptane ...                                | $C_7H_{16}$       | $CH_3-(CH_2)_3-CH(CH_3)-CH_3$ | 90°·3 C.  | $D_4^{20}$ 0.6969    |
| Normal octane ...                              | $C_8H_{18}$       | $CH_3-(CH_2)_6-CH_3$          | 125°·5 C. | $D_{20}^{20}$ 0.7185 |
| Iso octane ...                                 | $C_8H_{18}$       | $CH_3-(CH_2)_4-CH(CH_3)-CH_3$ | 119°·5 C. | $D_{20}^{20}$ 0.7190 |
| Normal nonane ...                              | $C_9H_{20}$       | $CH_3-(CH_2)_7-CH_3$          | 149°·5 C. | $D_{20}^{20}$ 0.718  |

| <i>Hydroaromatic hydrocarbons (C<sub>n</sub>H<sub>2n</sub>)</i><br>( <i>Cycloparaffins or naphthenes</i> ) |     |                                |   |            |                                     |
|--|-----|--------------------------------|---|------------|-------------------------------------|
| Cyclo-pentane-pentamethylene   |     | C <sub>5</sub> H <sub>10</sub> |  | 50°-5 C.   | D <sub>4</sub> <sup>20</sup> 0.7506 |
| Methyl-cyclo-pentane   | {   | C <sub>6</sub> H <sub>12</sub> |  | 72° C.     | D <sub>4</sub> <sup>21</sup> 0.7501 |
| Methyl-penta-methylene   |     |                                |   |            |                                     |
| Cyclo-hexane   | {   | C <sub>6</sub> H <sub>12</sub> |  | 79° C.     | D <sub>4</sub> <sup>0</sup> 0.7967  |
| Hexa-methylene   |     |                                |   |            |                                     |
| Hexa-hydro-benzene   | {   | C <sub>7</sub> H <sub>14</sub> |  | 94°-96° C. | D <sub>4</sub> <sup>0</sup> 0.780   |
| Methyl-cyclo-hexane  |     |                                |   |            |                                     |
| Methyl-hexa-methylene  | {   | C <sub>8</sub> H <sub>16</sub> |  | 80°-4 C.   | D <sub>0</sub> 0.899                |
| Hexa-hydro-toluene   |     |                                |   |            |                                     |
| <i>Aromatic hydrocarbons (C<sub>n</sub>H<sub>2n-6</sub>)</i>   |     |                                |   |            |                                     |
| Benzene  | ... | C <sub>6</sub> H <sub>6</sub>  |  | 110°-3 C.  | D <sub>4</sub> <sup>13</sup> 0.8708 |
| Toluene  | ... | C <sub>7</sub> H <sub>8</sub>  |  | 142° C.    | D <sub>0</sub> 0.8932               |
| Xylene   | ... | C <sub>8</sub> H <sub>10</sub> |  | 153° C.    | D <sub>0</sub> 0.8798               |
| Cumene   | ... | C <sub>9</sub> H <sub>12</sub> |  |            |                                     |

3. Iodine value.
4. Sulphur determination.
5. Purity (i.e., freedom from adulterants).

These may be regarded as the minimum requirements in a report on a petrol of which the source is unknown. In the case of known products the sulphur and iodine value determinations are not so essential because the properties investigated by those tests are well known for largely marketed products from established fields.

The further tests described in the following remarks are, some of them, of a confirmatory or alternative character, whereas others are of no interest whatsoever to the buyer but of value to the refiner or the student.

#### (c) Specific gravity

Taking into consideration the widely varying hydrocarbons quoted above and in many cases the closeness of their densities it will be seen that the specific gravity alone is no guide whatever as to the composition of a petrol.

It is of value, however, for calculating weight from volume and as a check on bulk spirit after transport if the quality has been predetermined by other tests described hereafter.

It is of interest to observe that certain aromatic hydrocarbons of specific gravities varying from 0.870 to 0.880 have the same boiling points as entirely different hydrocarbons of 0.700 to 0.760 specific gravity.

The determination of specific gravity can be made by means of the Westphal or Sartorius balance or with hydrometers.

The Sartorius balance shown in fig. 15 is useful for fairly small quantities of spirit such, for example, as those obtained from the fractional distillation of a sample; it is superseded to a great extent in practice by hydrometers which can be obtained to give sufficiently accurate readings for industrial and commercial purposes.

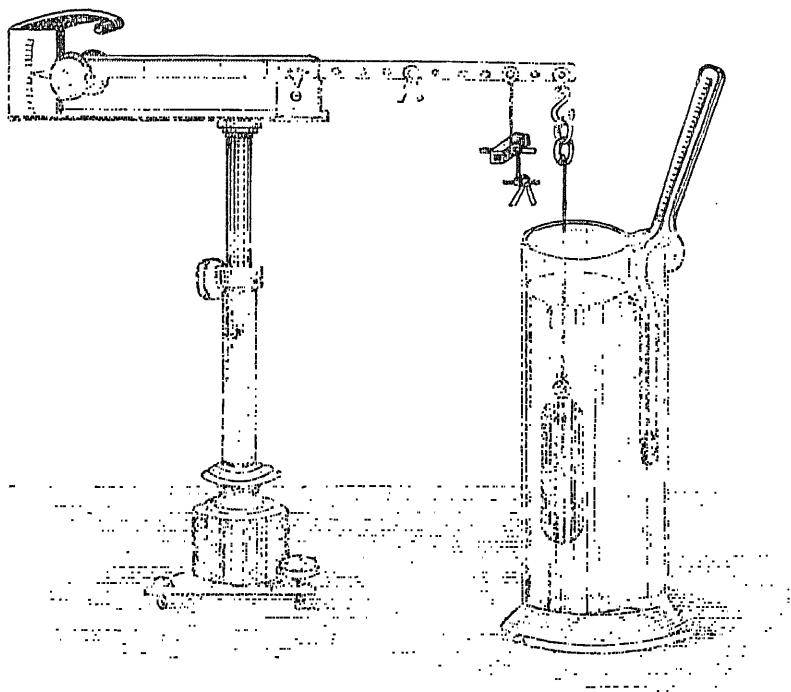


Fig. 15. Sartorius balance.

Fig. 16 shows a modified form of hydrometer in which a thermometer is situated inside the float, thus enabling a simultaneous reading of both temperature and density. The instrument might appropriately be called a thermohydrometer.

Specific gravity should be stated at 15° C. at which



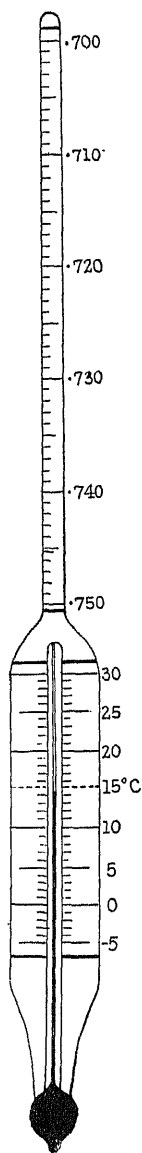


Fig. 16.  
Thermo-  
hydrometer.

temperature it represents the weight in grams of one cubic centimetre of the spirit.

It is often expressed at 60° F. (15°·6 C.) and sometimes at other temperatures.

Many government departments have accepted the 15° C. standard, so this is adhered to in this book except when otherwise stated.

Above this temperature a given weight of spirit will increase in volume and will show a lighter density, thus a correction must be applied to the reading at the higher temperature.

This correction for the sake of convenience is reckoned as 0·0008 per degree Centigrade, e.g.,

|                            |        |
|----------------------------|--------|
| Density observed at 18° C. | 0·7212 |
| Correction + (0·0008 × 3)  | ·0024  |
| Specific gravity at 15° C. | 0·7236 |

Since the correction coefficient of 0·0008 is not perfectly accurate and the error introduced by its use is increased as the temperature difference is greater, it is usual if the temperature of the petrol is far removed from 15° C. to warm or cool the spirit to within 10° or 15° C., i.e., 5° or 25° respectively.

Errors within 0·0015 may be accounted for as personal in the hydrometer method.

They may be due also to inaccuracy of graduation of the stem of the instrument or of the thermometer.

A further cause of differences is due to the meniscus formed at the point of contact of the hydrometer stem with the liquid. This is shown in fig. 17.

From this it will be seen that there are two distinct readings that can be made, one at *a*, where the liquid actually ceases to be in contact with the hydrometer stem, and the other at *b*, which is the point on the stem which is level with the surface of the liquid. It is usual to take the reading

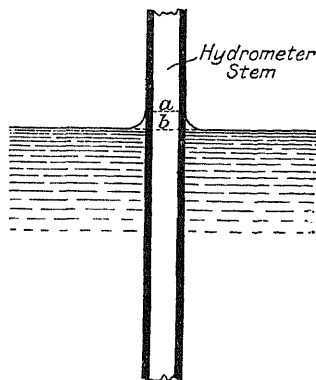


Fig. 17. Meniscus.

*b*. The difference between the two readings may be as much as 0.0005 on the average hydrometer scale and is partially attributable to personal differences in observation.

The temperature correction coefficient 0.0008 given above is sufficiently accurate for most commercial work. The table on page 60 shows the variation of this correction with the specific gravity of the oil to which it is applied.

To obtain weight in pounds per imperial gallon it is necessary to multiply the specific gravity by 10.

The great convenience of expression of specific gravity as the density, or weight of unit volume at 15° C., is realised particularly when working in litres and kilograms.

Thus 10,000 litres of benzine at 20° C. which has a density of 0.7182 at that temperature weighs 7182 kilograms and has a specific gravity of 0.7222 at 15° C.

Nevertheless in this country and in America and Canada it is still usual to refer to the specific gravity or density in degrees Baumé. There are regrettably various Baumé scales for the use of which the only advantage claimed, to the knowledge of the writer, is that decimal points are avoided!

Based originally on the density of salt solutions of varying concentration, the origin of some of the Baumé scales in use is clouded in mystery.

Furthermore it should be observed that the Baumé readings are usually rendered at 60° F. Now 60° F.

TABLE VIII.

*Density-temperature coefficients.*

| For a specific gravity of | Correction for one degree difference in temperature °C. |                   |
|---------------------------|---|-------------------|
|                           | Russian oils  | Pennsylvania oils |
| 0.700-0.720               | 0.00082   | 0.00086           |
| 0.720-0.740               | 0.00081   | 0.00082           |
| 0.740-0.760               | 0.00080   | 0.00077           |
| 0.760-0.780               | 0.00079   | 0.00072           |
| 0.780-0.800               | 0.00078   | 0.00068           |

is roughly 15°·5 C. so that many specific gravities are rendered at 15°·5 C.

A state of more ridiculous confusion in so elementary a matter can hardly be imagined.

For the time being it may be well to state that the expression of specific gravity as density at 15° C. proves in practice at least as satisfactory as any other method yet employed.

In considering the preparation of petroleum spirits from crude petroleum we have seen that various grades of spirit can be obtained, light and heavy,

varying in specific gravity from 0.650 to 0.760. All these fractions may be regarded as benzine or petrol,

TABLE IX.

*Baumé and specific gravity conversion table.*

| Baumé | Specific gravity | Baumé | Specific gravity | Baumé | Specific gravity |
|-------|------------------|-------|------------------|-------|------------------|
| 10    | 1.0000           | 44    | 0.8046           | 78    | 0.6730           |
| 11    | 0.9929           | 45    | 0.8000           | 79    | 0.6698           |
| 12    | 0.9859           | 46    | 0.7955           | 80    | 0.6666           |
| 13    | 0.9790           | 47    | 0.7909           | 81    | 0.6635           |
| 14    | 0.9722           | 48    | 0.7865           | 82    | 0.6604           |
| 15    | 0.9655           | 49    | 0.7821           | 83    | 0.6573           |
| 16    | 0.9589           | 50    | 0.7777           | 84    | 0.6542           |
| 17    | 0.9524           | 51    | 0.7735           | 85    | 0.6511           |
| 18    | 0.9459           | 52    | 0.7692           | 86    | 0.6481           |
| 19    | 0.9396           | 53    | 0.7650           | 87    | 0.6451           |
| 20    | 0.9333           | 54    | 0.7609           | 88    | 0.6422           |
| 21    | 0.9272           | 55    | 0.7568           | 89    | 0.6392           |
| 22    | 0.9211           | 56    | 0.7527           | 90    | 0.6363           |
| 23    | 0.9150           | 57    | 0.7487           | 91    | 0.6335           |
| 24    | 0.9091           | 58    | 0.7447           | 92    | 0.6306           |
| 25    | 0.9032           | 59    | 0.7407           | 93    | 0.6278           |
| 26    | 0.8974           | 60    | 0.7368           | 94    | 0.6250           |
| 27    | 0.8917           | 61    | 0.7329           | 95    | 0.6222           |
| 28    | 0.8861           | 62    | 0.7292           | 96    | 0.6194           |
| 29    | 0.8805           | 63    | 0.7254           | 97    | 0.6167           |
| 30    | 0.8750           | 64    | 0.7217           | 98    | 0.6140           |
| 31    | 0.8696           | 65    | 0.7179           | 99    | 0.6113           |
| 32    | 0.8642           | 66    | 0.7143           | 100   | 0.6087           |
| 33    | 0.8589           | 67    | 0.7107           | 101   | 0.6060           |
| 34    | 0.8537           | 68    | 0.7071           | 102   | 0.6034           |
| 35    | 0.8485           | 69    | 0.7035           | 103   | 0.6008           |
| 36    | 0.8433           | 70    | 0.7000           | 104   | 0.5983           |
| 37    | 0.8383           | 71    | 0.6965           | 105   | 0.5957           |
| 38    | 0.8333           | 72    | 0.6931           | 106   | 0.5932           |
| 39    | 0.8285           | 73    | 0.6897           | 107   | 0.5907           |
| 40    | 0.8235           | 74    | 0.6863           | 108   | 0.5882           |
| 41    | 0.8187           | 75    | 0.6829           | 109   | 0.5858           |
| 42    | 0.8139           | 76    | 0.6796           | 110   | 0.5833           |
| 43    | 0.8092           | 77    | 0.6763           |       |                  |

in the present sense of that term, but in their particular application in other industries some are given names that will be referred to under the heading "Uses."

(d) **Volatility and vapour pressure**

Petrol is completely volatile at ordinary temperatures so that a few drops left to evaporate on a watch glass should leave no residue if the spirit is pure.

A simple test sometimes applied is to evaporate a drop of the spirit on a clean filter paper; where no grease patch should remain, for the appearance of such a patch would indicate the presence of higher boiling-point products of a less degree of volatility than that desirable in a well refined spirit.

It is appropriate here to touch on the question of vapour pressure. At the surface of all liquids there is a pressure of the molecules of the liquid which is opposed to the pressure of the atmosphere. Some of these molecules may return to the liquid whereas others become lost in the atmosphere, the liquid suffering a loss known simply as evaporation.

If the temperature of the liquid be raised this molecular pressure or vapour pressure increases and the rate of evaporation is similarly increased. On further rise of temperature a point is reached where the vapour pressure is equal to the atmospheric pressure and at this point the liquid boils.

It would appear then, that a determination of the vapour pressure at various temperatures might be of use in examining a petrol sample.

In practice it is more convenient to record the boiling points in the course of a fractional distillation.

The test for vapour pressure is a simple physical determination and is accomplished as follows:

A stout glass tube 1 metre in length and 10 mm. in diameter is filled with mercury from which the air has been expelled by previous boiling.

The tube is then inverted in a cup of air-free mercury and the height of the mercury column below the Torricellian vacuum noted. A small quantity of the spirit is introduced through the bottom of the tube by means of a curved pipette.

It is advisable to incline the glass tube when introducing the liquid to avoid the effects of the violent evaporation of the spirit.

The vapour pressure of the petrol, of which excess should be present, depresses the mercury column. The amount of depression should be recorded. The depression in millimeters is a direct reading of the vapour pressure at that temperature. By jacketting the mercury tube determinations can be made at any temperature desired.

For the pressure of the small amount of liquid above the mercury a correction is made, thus the factor,

$$\frac{h \times S}{13.6}$$

(where  $h$  is the height of the excess liquid and  $S$  its specific gravity) must be subtracted from the difference obtained above.

At higher temperatures a correction is also applied for the pressure of mercury vapour.

Vapour pressure is expressed in millimeters of mercury. Normal atmospheric pressure is 760 millimeters.

It is stated that Californian petrol of 0.714 will evaporate at ordinary temperatures more readily than a light Pennsylvanian spirit of 0.667 and again a petrol of 0.725 to 0.737 from the mid-continent crude has a lower initial boiling-point than a 0.680 spirit from the Pennsylvanian crude, or, in general, gasoline

from mid-continental and western fields is more volatile for a given specific gravity than that obtained from eastern fields.

Ballantyne has described a method of estimating the dissolved gases in petrol and, in view of the introduction of casing-head gasoline, this method would at first sight appear to be useful.

TABLE X.  
*Vapour pressure of petrol.*

| Temperature | I (Brame) | II (Brame) | III (Kent) |
|-------------|-----------|------------|------------|
| 0° C.       | 90 mms.   | 54 mms.    | 99 mms.    |
| 10          | 144       | 95         | 133        |
| 20          | 204       | 136        | 179        |
| 30          | 287       | 211        | 251        |
| 40          | —         | —          | 360        |
| 50          | —         | —          | 493        |
| 60          | —         | —          | 648        |

A reduction in the pressure over mercury in a nitrometer tube is the process. A minus pressure of 10 inches is judged to be sufficient.

Then, if the sample yields no more than 1 cc. of gas after fifteen minutes it is regarded as free from gaseous additions.

TABLE XI.  
*Dissolved gases in petrol.*

| Difference in mercury level | Volume of gas at 15°·5 C. and pressure stated yielded 10 ccs. of spirit |                     |       |                       |         |
|-----------------------------|---|---------------------|-------|-----------------------|---------|
|                             | Pratt's   | Pratt's 4 years old | Shell | Pratt's and acetylene | Benzene |
| 5"                          | trace   | trace               | trace | 0·5                   | nil     |
| 10                          | 0·8   | 0·7                 | 0·5   | 3·6                   | nil     |
| 15                          | 2·6   | 2·6                 | 2·6   | —                     | trace   |
| 20                          | 6·0   | 7·2                 | 7·8   | 13·0                  | 1·4     |

It is thought, however, that the test is superfluous if a fractional distillation is carried out since this

latter test readily indicates any appreciable quantities of highly volatile constituents.

Ballantyne has given the results of the test on commercial products as shown in Table XI.

When considering questions of storage and bulk transport it is necessary to take into account the vapour pressure of the spirit handled.

In the case of filling steel drums for transport of spirit it is usual to leave a space of at least 5 % empty.

### (e) Fractional distillation

The fractional distillation of a petrol sample is a means of determining the percentage content in high and low boiling-point products; it constitutes therefore an indication to the volatility of the sample examined. It is further a guide to the homogeneity of the sample and will detect the presence of "naphtha bottoms" or "kerosene tails" which are liable to remain in badly rectified spirit. No difference is exhibited, however, on distillation test between cracked and straight-run products.

At the best, the methods of fractional distillation employed in technical analysis are but arbitrary; nevertheless, if the apparatus used be standardised and the mode of operation be always in accordance with an established procedure, results are obtained that are reasonably constant for the same sample and sufficiently accurate to determine the good or bad points of that sample.

The methods in general use to-day are those devised by Redwood and by Engler.

The following description of the Redwood distilla-



tion test is given (by kind permission) in the words of its author<sup>1</sup>.

"100 cc. of the spirit is placed in a Wurtz flask supported on a sand-dish and connected with a Liebig condenser. The bulb of the flask is  $2\frac{3}{4}$  inches in diameter, the neck  $\frac{3}{4}$  inch in diameter by  $5\frac{3}{4}$  inches in length, and the exit tube is  $2\frac{1}{2}$  inches above the shoulder. The tube of the Liebig condenser is 24 inches in length. The thermometer inserted through the cork in the tubulure is at first so adjusted that its bulb is just immersed in the spirit, and as soon as the ebullition becomes active it is gradually raised, so that the bulb is slightly below the rising level of the vapour (which can be seen in a bright light). The temperature at which the first drop of distillate falls from the end of the exit tube of the flask into the condenser is noted as the initial boiling-point of the sample. The percentages collected in a 100 cc. measure glass up to specified thermometer-readings are recorded, and the temperature at which the flask becomes dry is noted as the final boiling point."

The Engler method as originally devised was intended primarily for the distillation of crude oil. The method has been slightly modified by Ubbelohde. The following description is translated in Redwood's *Treatise on Petroleum*, II. 208, from a paper by Kissling.

The dimensions of the Engler flask are shown in fig. 18 and the complete apparatus assembled is shown in fig. 19.

"A distilling flask (the Engler flask, fig. 18) is charged with 100 cc. of the benzine to be tested, and connected with a Liebig's condenser 60 cm. in length, which discharges into a measuring glass graduated to

<sup>1</sup> Sir Boverton Redwood, *Treatise on Petroleum*, C. Griffin & Co., II. 207.

$\frac{1}{2}$  cc. The flask is supported by wire gauze such as is used in the filter-presses of sugar-refineries. At the beginning of the operation it is advisable to let the bent end of the adapter dip as far into the glass as

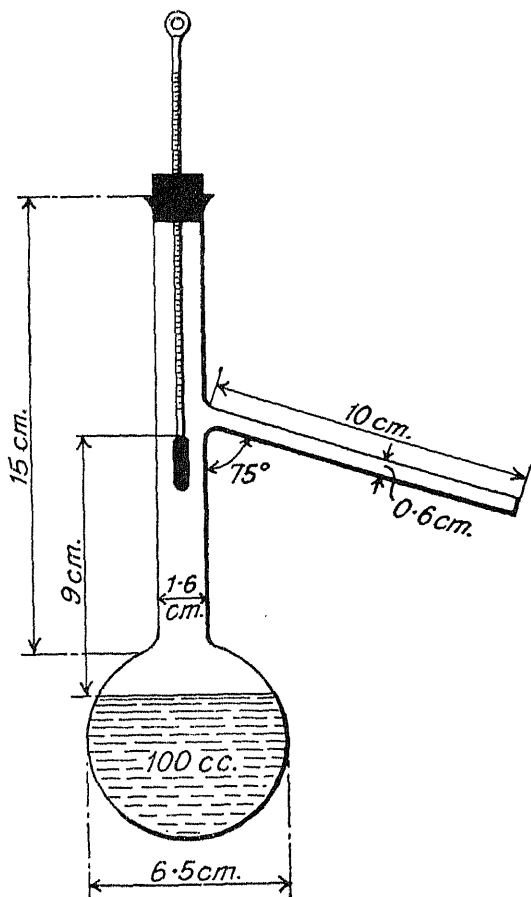


Fig. 18. Engler flask.

possible, to minimise the evaporation of the lightest fractions. The rate of distillation recommended is 2 to  $2\frac{1}{2}$  cc. per minute. At first the temperature usually rises rapidly, then more slowly, until it

reaches a point where it remains practically stationary. This is the 'lower boiling limit' of the benzine under examination.

At every rise of  $10^{\circ}$  from this point (beginning with the first even  $10^{\circ}$ ) the volume of distillate is read off. Finally, when the bottom of the flask is free from liquid, a Bunsen flame is applied, and the temperature registered is considered as the 'upper limit' of boiling. For this it is not necessary to drive off the last

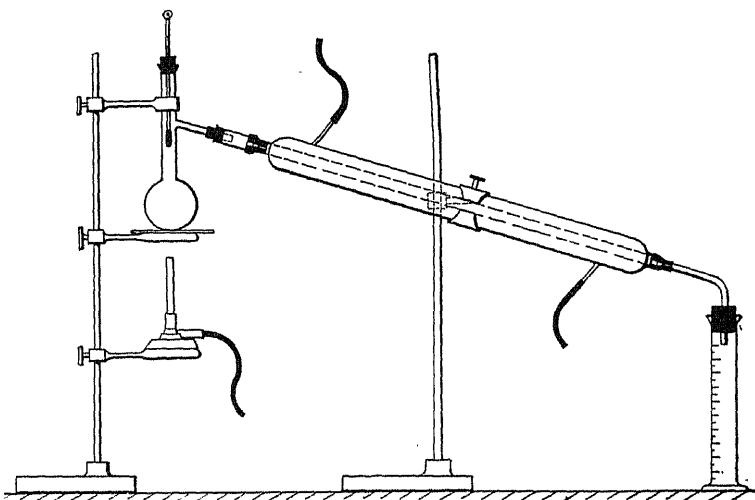


Fig. 19. Distillation apparatus.

high-boiling portions (which at most amount to 0.1 to 0.2 per cent.). To ascertain their boiling-points, the thermometer must be lowered to the bottom of the neck of the flask."

Further details of the Engler method as used in this country are as follows: the rate of distillation timed as 2-2.5 ccs. per minute is roughly equivalent to two drops per second. The initial boiling-point is registered as two temperatures, (a) temperature at which first drop falls from flask into condenser, and

(b) temperature at which first drop falls from condenser into receiving cylinder.

The upper boiling-point limit is taken as that temperature at which the bottom of the flask becomes dry, at this temperature only vapour is in the flask and the spirit is completely volatile. The thermometer is not lowered as described in the above translation.

It is usually assumed that the distillation test is undertaken at normal barometric pressure, i.e., 760 millimeters.

If the barometer pressure is 5 millimeters or more from the normal, either above or below, a correction should be applied for the increase or decrease respectively of the atmospheric pressure.

The correction is made by taking the difference between the boiling point of pure water at the normal barometric pressure and the pressure recorded during the test<sup>1</sup>.

Instead of reading the percentage distillate from the sample at the even 10° C. (i.e., 60°, 70°, 80°, etc.) the reading should be made at temperatures higher or lower as the case may be by the difference between the boiling-points of water.

Thus, assuming a barometric pressure of 775 mms. at which the boiling-point of water is 100°·55 C., the percentage distillate of the sample as for 80° C. should be read at 80°·55.

It is not usual to make this correction in daily routine testing but it is certainly better practice always to record the barometric pressure at the time of carrying out the test.

<sup>1</sup> See Table XXVIII, Appendix.

Lomax<sup>1</sup> has recently described a method he has devised for which he claims speed of manipulation

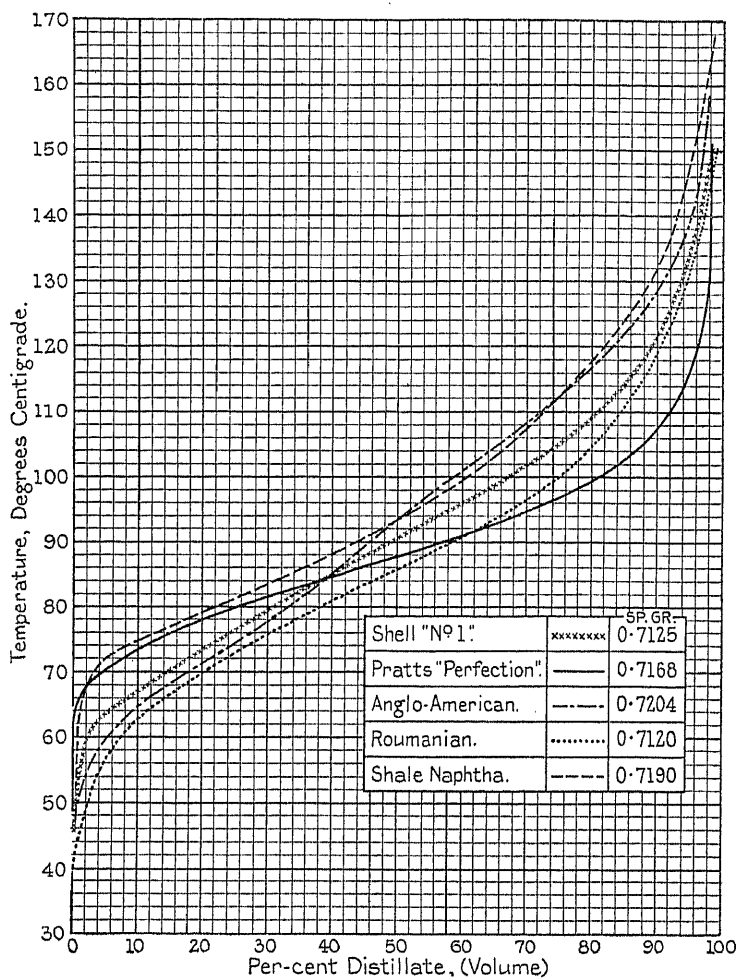


Fig. 20. Petrol distillation graphs.

combined with accuracy of results. The following description is taken from his paper:

"The apparatus consists of a small round-bottom

<sup>1</sup> *J. Inst. Pet. Tech.* IV. 1917.

flask of  $2\frac{1}{2}$  in. diameter, the inside diameter of the neck being 1 in., and its length from the shoulder  $1\frac{1}{2}$  in. To this flask, by means of a sound, well-fitting cork, is attached a 4-pear Young dephlegmator column of total length  $12\frac{3}{8}$  in., length from bottom to side-arm  $10\frac{3}{8}$  in., the beginning of the bottom pear being  $3\frac{1}{2}$  in. from the bottom of the column, and the total length of the 4 pears being  $5\frac{3}{8}$  in. The inside diameter of the tube from which the column is made is  $\frac{7}{16}$  in., and the diameter of the pears is  $1\frac{1}{4}$  in. The side tube is bent at an angle of approximately  $70^\circ$ , and is  $7\frac{1}{4}$  in. in length. The distillation apparatus is attached to an ordinary Liebig condenser, 22 in. long, fitted with an adapter, to lead the spirit into the 100 cc. graduated reception-cylinder. An accurate thin-stem, small-bulb thermometer is fitted in the top of the column, the top of the bulb of the thermometer being level with bottom of the side-arm. The column is enclosed in a wide tube 8 in. long by 2 in. diameter, the bottom of which is fitted on to a cork, butting on to the cork connected to the flask, while the top of the tube is loosely packed with cottonwool. This wide tube serves to protect the column from draughts, and provides a very efficient air-lagging. It was suggested by a column designed for a different purpose by Mr F. Esling, which was protected in a similar manner. In making the test, the column, with its protecting tube, is fitted to the flask, into which have been placed a few small pieces of boiling pot, and then 100 cc. of the spirit to be tested is charged in by means of a pipette through the top of the column. The side tube is now connected to the condenser, and heating of the flask (which is protected by plain iron gauze) is commenced. A little practice soon

enables one to estimate the size of flame necessary to bring the liquid to boiling-point at the desired rate.

The initial boiling-point is taken as that at which the first drop falls from the side-arm. The distillation is continued at the rate of 2.5 cc. per minute. This rate is conveniently timed by means of a metronome, the beat of which has previously been calibrated so that, at the rate of one drop per beat, the distillation will be at the required rate.

Readings of the distillates may be taken at any desired points, but for most practical purposes the amounts volatile below 100° C., 125° C., and 150° C., together with the total amount volatile, are all that are necessary. The final boiling-point is taken as that at which the flask becomes dry, which is usually accentuated by the formation of a white cloud of vapour as a drop from the column falls on the hot bottom of the flask."

In spite of the advantages claimed by Mr Lomax for his method it is only fair to the Engler test to state that for general routine examination the latter is undoubtedly sufficiently accurate and the results obtained by different operators are sufficiently in agreement for practical purposes. In a more careful examination of a petrol, it is desirable sometimes to distil a larger quantity than 100 ccs. (e.g., 500–1000 ccs.), in which case each fraction is large enough for a determination of specific gravity and the distillation characteristics of the spirit are more readily observed.

Furthermore, in accurate testing a dephlegmator is employed with the larger quantities.

This additional apparatus acts in the same way as the columns used in the refinery (see page 32).

Various forms of dephlegmators or still-heads are in use and are fully described in S. Young's *Fractional Distillation*. The dephlegmators used in petrol distillations are shown in figs. 21 and 22 and they are

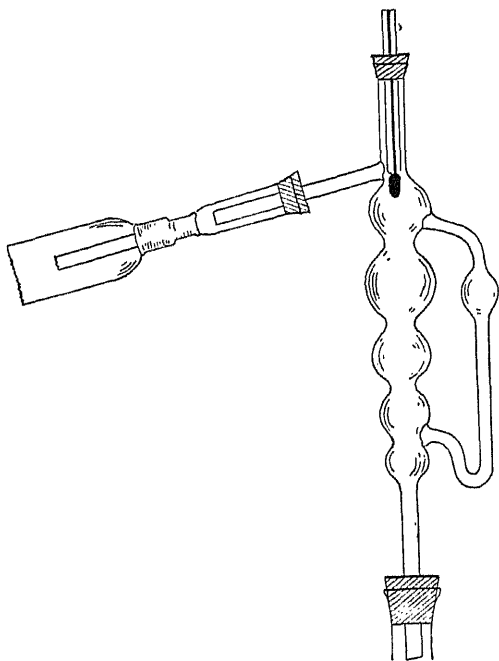


Fig. 21. Glinsky dephlegmator.

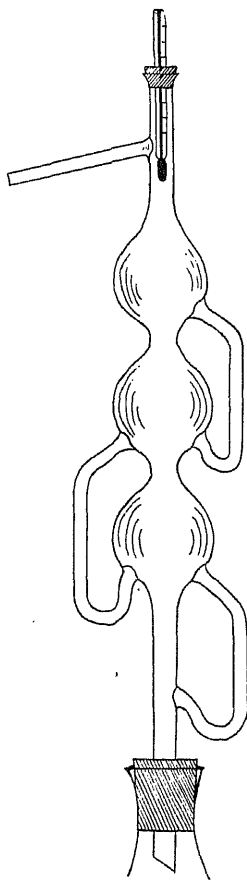


Fig. 22. Le Bel-Henninger dephlegmator.

known by the names of their designers who are Glinsky and Le Bel-Henninger respectively.

Other precautions necessary in accurate work in-



clude the correction for the partial immersion of the thermometer employed (if this is not already allowed for on the thermometric scale) and a reading of the barometric pressure at which the test is made.

In a recent paper Dean recommends the following method which is here quoted in his words:

“The flask used shall be the standard 100 cc. Engler flask, described in the various text-books on petroleum. The dimensions are as follows:

|                         | cm.      | ins. |
|-------------------------|----------|------|
| Diameter of bulb        | ... 6.5  | 2.56 |
| Diameter of neck        | ... 1.6  | 0.63 |
| Length of neck          | ... 15.0 | 5.91 |
| Length of vapour tube   | 10.0     | 3.94 |
| Diameter of vapour tube | 0.6      | 0.24 |

Position of vapour tube, 9 cm. (3.55 in.) above surface of oil when the flask contains its charge of 100 cc. The tube is approximately in the middle of the neck.

The flask shall be supported on a ring of asbestos having a circular opening  $1\frac{1}{4}$  in. in diameter; this means that only this limited portion of the flask is to be heated. The use of a sand bath is not approved.

The condenser shall consist of a thin-walled tube of metal (brass or copper),  $\frac{1}{2}$  in. internal diameter and 22 in. long. It shall be set at an angle of  $75^\circ$  from the perpendicular and shall be surrounded with a water jacket of the trough type. The lower end of the condenser shall be cut off at an acute angle and shall be curved down for a length of 3 in. The condenser jacket shall be 15 in. long.

The accuracy of distillation primarily depends on the accuracy of the thermometer and on this account the instrument should be so defined that the results of

different analysts may check. The thermometer described in the report of the American Society for Testing Materials is not adapted for use with gasoline, its range being unnecessarily high and the lower temperatures being difficult to read because of interference from the cork in the neck of the distillation flask.

The present discussion does not deal with the details of temperature measurement but simply indicates requirements that should be met and will ensure that the maximum possible variations in thermometer readings at different analytical laboratories cannot exceed  $1^{\circ}$  or  $2^{\circ}$  C.

Briefly, the thermometer should be an accurate 'nitrogen-filled' instrument with a short bulb (length, 10 to 15 mm., 0.39 in. to 0.59 in.) and with the mark for  $35^{\circ}$  C. ( $95^{\circ}$  F.) at a distance between 100 and 120 mm. (3.94 in. to 4.73 in.) from the top of the bulb. The thermometer should be scaled for total immersion.

The above requirements insure that almost always the lowest temperatures registered may be read above the cork of the distillation flask, and variations because of the so-called 'stem correction' will always be practically the same. The stem correction should not be applied, but it should be understood that results of distillations are expressed in terms of thermometer readings, not of actual temperatures. The use of partial-immersion thermometers is not recommended for distillations, as these instruments are no more likely to agree with one another than are the more common total-immersion thermometers.

The following specification for a gasoline distillation thermometer is offered so that the prospective purchaser may be able to state definitely what he

requires, and by so doing obtain a satisfactory instrument. The specification has been submitted to several manufacturers of thermometers, who state that it insures the obtaining of a satisfactory high-grade instrument without imposing on the maker unnecessary and troublesome restrictions that increase the cost.

The thermometer should be made of selected enamel-backed tubing, having a diameter between 5.5 and 7 mm. The bulb should be of Jena normal or Corning normal glass; its diameter shall be less than that of the stem, and its length between 10 and 15 mm. The total length of the thermometer should be approximately 380 mm. The range should cover 0° to 270° C., with the length of the graduated portion between the limits of 210 and 250 mm. The point marking a temperature of 35° C. should be not less than 100 nor more than 120 mm. from the top of the bulb.

The scale should be graduated for total immersion. The accuracy must be within about 0.5° C. The space above the meniscus must be filled with an inert gas; such as nitrogen, and the stem and bulb must be thoroughly aged and annealed before being graduated.

All material and workmanship must be of the best. The scale shall be marked for single-degree intervals. Each tenth degree shall be numbered and each fifth degree distinguished by a longer mark.

The flask connected with the condenser shall be filled with a 100 cc. charge of gasoline, which shall be measured from a 100 cc. graduated cylinder. The same cylinder may be used without drying as the receiving vessel for the distillate. Heat shall be applied to the flask in regulated degree, care being taken that

the whole distillation from beginning to end shall proceed at a rate of not less than 4 cc. nor more than 5 cc. a minute. Readings of the thermometer shall be made as each 10 per cent. distills.

The dry point or highest temperature reading at the end of the distillation shall also be recorded. The distillation loss shall be determined by adding the percentage of residue in the distilling flask, after cooling, to the percentage of total distillates held in the receiver. If the distillation loss is over 3 per cent., a check distillation shall be made, as excessive loss may indicate that the rate of distillation at the beginning was too rapid. In case the magnitude of the loss is confirmed, this fact is of importance in indicating that the gasoline contains very volatile constituents, particularly those derived from added casing-head gasoline.

The condenser trough shall be filled with a mixture of cracked ice and water (not dry cracked ice), and during the distillation sufficient ice shall be kept in the trough to prevent the temperature of the cooling water exceeding 8° C. (46° F.).

If distillations are made at high altitudes, or when barometric pressures are low, allowances may be made for this factor. In general, recording the barometric pressure read at the time of the distillation will suffice, and it is recommended that whenever there is possibility of dispute over the results of a distillation this should be done.

The thermometer bulb should be covered with a thin film of absorbent cotton; this keeps the glass always wet with the condensate from the vapour and thus prevents possible fluctuations in the temperature. It also tends to prevent superheating of the

bulb at the end of the distillation and thus makes possible an accurate determination of the dry point.

The whole procedure is relatively simple, but involves certain details of manipulation of more or less importance. The use of apparatus at least approximately as described is essential, although the method is such that no considerable discrepancies will result if the apparatus is not exactly standard. The chief source of difficulty is the rate of heating. It is, of course, desirable to bring the initial charge up to the boiling point as rapidly as possible in order not to waste time, but unless care is taken, the distillation will start too rapidly and there will be losses in the form of uncondensed vapour. In consequence the actual percentages will be higher than those read, and the temperatures may likewise be noticeably high. If, however, the distillation loss is not permitted to exceed the stated amount, this difficulty can be avoided. In case the gasoline to be tested contains considerable proportions of constituents difficult to condense, the condenser trough may be filled with a freezing mixture and the receiver also kept cooled. If this is done, it is desirable to measure out the original charge at the temperature of this freezing mixture in order to avoid discrepancies due to changes of volume with temperature."

In another recent attempt at the standardisation of petrol testing it is suggested that 200 ccs. be distilled in the Engler flask (larger size of same proportions) it is stated that with 100 ccs. the errors due to lag of distillate in the condenser and those due to misreading of volumes are relatively too great. A thermometer corrected for partial immersion should be used or a correction should be applied and the

barometric pressure should be recorded. The first distillates should be collected in iced water and the temperature of the condenser water throughout the distillation should not exceed  $6^{\circ}\text{C}$ .

Anfilogoff<sup>1</sup> describes yet another variation of the distillation-test which he has devised to meet the combined demands of speed and accuracy.

In conclusion it should be stated that in the petroleum laboratories of this country either the Redwood or the Engler method is in general use.

### (f) **Calorific value**

The calorific value or calorific power of an oil gives an indication of its value as fuel in so far as it is a measure of the number of heat units that can be obtained by combustion of unit weight of that oil.

The unit of heat in this country is the British Thermal Unit (B.T.H.U.) and is the amount of heat required to raise the temperature of 1 lb of pure water by  $1^{\circ}\text{F}$ . or from  $39^{\circ}\cdot 1\text{ F}$ . to  $40^{\circ}\cdot 1\text{ F}$ .

The scientific unit is the "calorie" which is the amount of heat required to raise the temperature of 1 gram of pure water through  $1^{\circ}\text{C}$ . (from  $0^{\circ}\text{C}$ . to  $1^{\circ}\text{C}$ .).

Having regard to the variations in composition of petrols from different sources it is remarkable to what a relatively small degree their calorific values vary. This practical constancy renders it unnecessary to carry out the determination of calorific value with any frequency.

It is nevertheless occasionally desirable.

The calorific value of a substance is determined by burning a known weight of it in an atmosphere of compressed oxygen contained in a bomb.

<sup>1</sup> *J. Soc. Chem. Indust.* Jan. 1918.

The heat produced is measured by noting the rise in temperature of the water contained in a calorimeter in which the bomb is completely immersed.

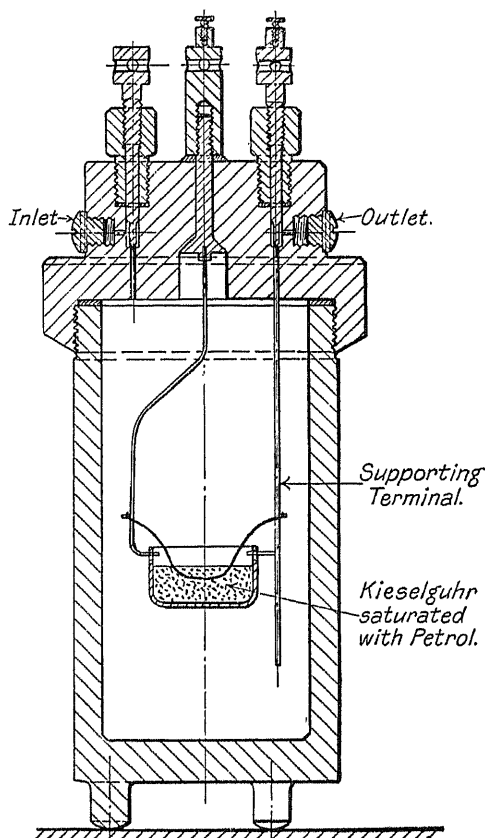


Fig. 23. Bomb.

The apparatus employed for the determination consists essentially of the following portions:

**Bomb.** This consists of a strong cylindrical nickel vessel shown in fig. 23 of about 300 ccs. capacity and is lined with either platinum, enamel or gold. It is fitted with a screw-on head furnished with an inlet

valve and two electric terminals. One of the latter is connected with a support extending well down into the bomb, which acts also as the main support of the capsule in which the fuel is placed.

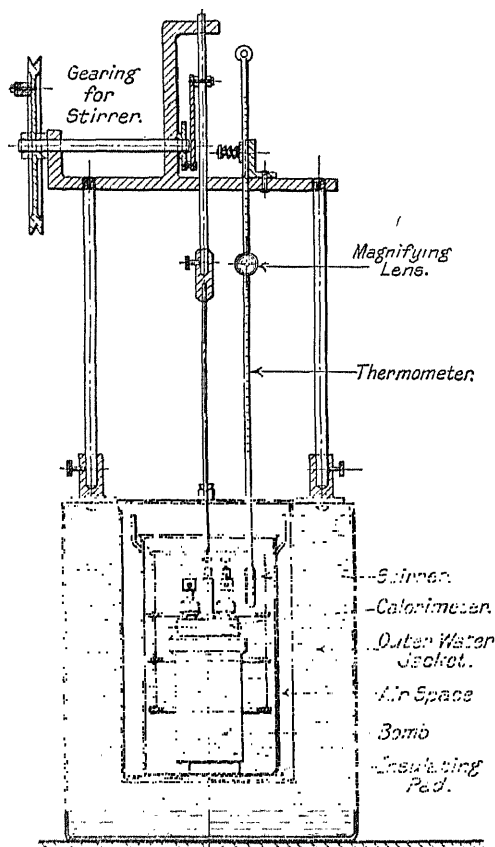


Fig. 24. Calorimeter.

**Calorimeter.** This is shown with the bomb in place in fig. 24. It consists of an ordinary copper cylindrical calorimeter sufficiently large to contain the bomb and an encircling stirrer.



The latter can be given a vertical motion by means of a geared device worked by a small electric motor. A known weight of distilled water is used in the calorimeter and the latter rests on insulating material and is surrounded by an outer water jacket.

**Thermometer.** This should be exceedingly delicate and should be graduated to 1/100th degrees. A lens should be used for taking the readings.

**Battery, etc.** A series of storage cells capable of giving a current of 2 amps. at 8-10 volts should be employed with starting key for making connection.

**Practical determination.** About one gram of the substance is accurately weighed out into a small platinum or silver capsule. The capsule should be previously half filled with dry Kieselguhr to act as an absorbent and the weighing must be done with the capsule covered with a well fitting watch glass.

Meanwhile a loop of platinum wire is fixed between the terminal supports of the capsule and a current is passed for a few seconds to make sure that the ignition device is in order. In addition a known weight, about 2000 grms. of distilled water is placed in the calorimeter.

The capsule containing the fuel is now quickly transferred to its position on the terminal supports of the bomb-head, the platinum loop is arranged to dip into the Kieselguhr and the bomb-head is screwed on to the bomb. Oxygen is then slowly introduced into the latter from a cylinder until the pressure in the bomb is 25 atmospheres; the valve is now closed and the cylinder disconnected. The bomb is now placed in the calorimeter, the water of which should completely cover it, the thermometer is fixed in position and the stirring device started. Care should be taken

to notice whether there is any leakage of oxygen from the bomb.

After a short time the temperature is noted, the readings of the thermometer being repeated at minute intervals for five minutes. At the end of the fifth interval, the fuel is ignited by depressing the key of the battery circuit. The heat evolved by the combustion is transmitted to the water in the calorimeter the temperature of which is noted on the thermometer at minute intervals during the period of combustion, i.e., until a maximum temperature is reached. This usually takes about 5 minutes. During the succeeding cooling period the readings are taken at similar intervals for a further period of five minutes.

From the observations made the following should be obtained.

$T$  = rise in temperature of calorimeter (corrected).

$W$  = weight of petrol in grams.

$x$  = weight of water in calorimeter in grams.

$y$  = water equivalent of calorimeter in grams.

$l$  = latent heat of condensed steam from the fuel.

Then the calorific value of the sample is equal to

$$\frac{T(x+y)}{W} - l \text{ calories} \dots\dots\dots(1).$$

**Corrections.** (a) *Radiation.* During the experiment heat is absorbed or lost by radiation. This can be corrected for by means of the following formula which is a simplification of the Regnault-Pflaundler formula:

$$t' = mv_{\Delta} + m \frac{(n_{\Delta} + v_{\Delta})}{2} \dots\dots\dots(2),$$

where  $t'$  = required temperature correction.

$m$  = period of combustion in minutes.

$n_{\Delta}$  = fall in temperature per minute in final period of cooling.

$v_{\Delta}$  = fall in temperature per minute in initial period before combustion.

Then, in the first equation (1) for calculating the result,  $T' = t + t'$ , where  $t$  is the observed rise in temperature.

(b) *Water Equivalent of Calorimeter.* This is determined by burning a known weight of a substance of known calorific value (e.g., benzoic acid : 6333 calories) in the bomb and observing the temperature rise.

Then

$$Y = \frac{a(6333 + l)}{T} - x \dots\dots\dots(3)$$

where  $Y$  = water equivalent of calorimeter in calories.

$a$  = weight of benzoic acid in grams.

$T$  = temperature rise (corrected).

$x$  = weight of water in calorimeter in grams.

$l$  = correction for condensed water.

(c) *Condensed Steam.* The water formed by the combination of the hydrogen in the fuel with the oxygen in the bomb gives up its latent heat on condensation. This gives a fictitiously high temperature rise and in order to correct for this error a quantitative estimation of the water in the bomb must be made. The bomb is connected with a series of drying towers, and calcium chloride tubes as in the fig. 25.

The bomb is placed in an oil bath and is kept at  $105^{\circ}\text{C}$ . while a current of dry air is passed through it. The gain in weight of the calcium chloride tube gives the amount of water.

The correction is 600 calories for every gram of water formed and the deduction of this figure gives the net calorific value.

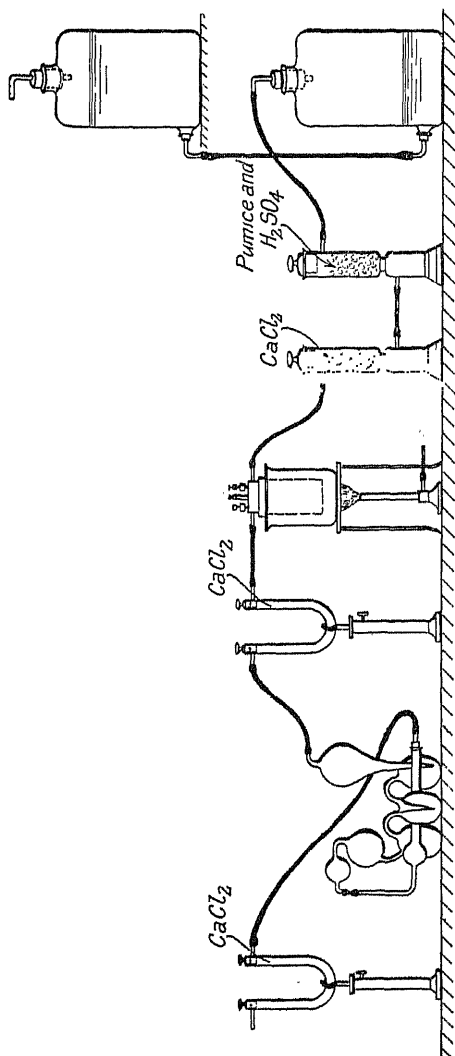


Fig. 25. Drying towers.

(d) If iron wire is employed instead of platinum to start the combustion a correction must be applied for

the heat evolved by the burning iron. Heat developed by one gramme of burning iron = 1600 calories.

Blount has recorded the calorific values of many samples of petrol fuel examined as varying between 20,092 and 20,344 B.T.H.U. per pound.

The following table shows within what normal limits the calorific values of a similar series of petroleum products lie, graduated according to their specific gravities.

TABLE XII.  
*Density-calorific value table.*

| Density at 15° C. | Calorific value in calories per gram |
|-------------------|--------------------------------------|
| 0.700–0.750       | 11,700–11,350                        |
| 0.750–0.800       | 11,350–11,100                        |
| 0.800–0.850       | 11,100–10,875                        |
| 0.850–0.900       | 10,875–10,675                        |
| 0.900–0.950       | 10,675–10,500                        |

From the above it will be observed that there is a tendency for the oils to show an increase in calorific value with a decrease in specific gravity.

This does not apply to any number of oils but to a series from the same crude.

Sherman and Kropff<sup>1</sup> have proposed this formula to express the relationship between specific gravity and calorific value of American petroleum products.

B.T.H.U.'s =  $18,650 + 40$  (Baumé degrees – 10).

In the case of commercial petrois, however, the variation between the highest and lowest values recorded does not exceed 1.5 %.

Furthermore, although the calorific value expresses

<sup>1</sup> *J. Amer. Chem. Soc.* xxx. 1626 (1908).

the number of heat units available only a certain proportion, depending on the thermal efficiency of the engine, are converted into useful work.

In the case of the internal-combustion engines used in automobiles and aeroplanes the thermal efficiency is from 20 to 26 %. Borlase Matthews<sup>1</sup> gives the figure as 18 % and Moore gives for automobile engines 22 % and aero-engines 27 %.

Certainly higher figures have been recorded but it must be remembered that the factors to be considered are innumerable and that the results are only approximate. One point of interest may be mentioned in this connection.

The lubricating oil used on these engines undoubtedly burns during the course of the explosions and so gives up a certain number of heat units, but the difficulty of determining the small proportion of heat generated in this way may well be imagined.

Since, then, the calorific value per unit weight of petrol may be taken for nearly all practical purposes as being a constant, the variation not exceeding 1.5 % as stated above, and further, that only some 25 % of those heat units available are actually converted into useful work, it would appear advantageous for the buyer of petrol who pays by the gallon to purchase the heavier grades of spirit.

The heavier grades of higher specific gravity and therefore greater weight per gallon evolve on combustion a larger number of heat units per gallon. This is, of course quite contrary to actual practice where the highest price is obtained for the lightest spirits, therefore a word of explanation is necessary.

With the heavier spirits there is usually found a

<sup>1</sup> *Aviation Pocket Book*, 1917.

low percentage of low boiling-point products, thus difficulties of starting up are likely to occur unless the spirit is blended to avoid this.

The above remarks go to show the reason for the increased mileage per gallon obtained with 'cracked' spirits which, for equal range of boiling-points, exhibit a higher specific gravity than the corresponding straight-run refinery petrol.

In fuel calculations it is often convenient, though for petrol not scientifically accurate, to estimate the calorific value from the elementary composition of the substance dealt with.

In the case of petrol the percentage composition may be taken to approximate to 84 % carbon and 16 % hydrogen, that is, to the composition of heptane,  $C_7H_{16}$ .

Now the calorific value of carbon is 14,600 B.T.H.U. and that of hydrogen 62,000 B.T.H.U., so that in 100 lb. of heptane there are

84 lb. of carbon giving  $84 \times 14,600$  1,226,400 B.T.H.U.  
and 16 lb. of hydrogen giving

|                    |     |     |     |           |    |
|--------------------|-----|-----|-----|-----------|----|
| 16 $\times$ 62,000 | ... | ... | ... | 992,000   | ,, |
|                    |     |     |     | 2,218,400 | ,, |

So that from 1 lb. of heptane one would expect 22,184 B.T.H.U. and this figure is known as the gross calorific value.

It must be remembered, however, that the products of combustion of this substance leave the engine at a high temperature and that the water formed by combination of the hydrogen with the oxygen of the air is in the form of steam.

The heat required to change the state of water from the liquid to steam is roughly 970 B.T.H.U. per lb.

of water, so that for every lb. of steam 970 B.T.H.U. must be subtracted from the above value as being unavailable for the purposes of useful work.

16 lb. of hydrogen require 128 lb. of oxygen for their complete combustion so that 144 lb. of steam are formed, thus:  $970 \times 144 = 139,680$  B.T.H.U. are carried away in the steam from 100 lb. of the fuel, that is, 1397 B.T.H.U. per lb., thus

$$22,184 - 1397 = 20,787 \text{ B.T.H.U.}$$

which would appear to represent the total heat units available and is known as the nett calorific value.

Strictly speaking a further deduction is necessary to account for the heat of formation of the compound. This explains the excess of the calculated value over the figure obtained by experiment.

### (g) Sulphur content

Although sulphur may be considered as a deleterious ingredient of petrol, it is seldom found in the finished products in sufficient quantity to cause any trouble beyond an unpleasant engine exhaust which is attributed to its presence.

This is due primarily to the fact that the sulphur is much less harmful than is generally supposed, and further, what sulphur there may be in the crude oil tends to concentrate in the heavier distillates.

From a large collection of representative samples (over 50 in number) the U.S. Bureau of Mines finds that the percentage of sulphur in commercial petroleum spirits of America varies from 0.01 % to 0.05 %. This small quantity is regarded as negligible.

Many commercial petrols fail to show any traces of



sulphur on the application of the usual tests, so that, in cases of doubt it is necessary to test only qualitatively in the first instance.

A small quantity of petrol boiled for a few minutes in a solution of ammonia should show no brown colouration on addition of silver nitrate solution. Another test is to boil a small quantity of the sample with a scrap of metallic sodium. When cool, water is added and in the resultant aqueous solution a drop of sodium nitroprusside should give no purple-violet colouration; similarly the aqueous solution should show no brown stain when placed on a bright silver coin.

The quantitative estimation of sulphur in petrol is most conveniently determined by examination of the aqueous solution of the products of combustion in the bomb-calorimeter after a calorific value has been taken.

The solution is treated with barium chloride and the sulphur estimated from the precipitated barium sulphate.

Moore has recently expressed the following opinions: "The corrosive action of sulphur contained in liquid fuels has been greatly exaggerated. Experience has shown that the products of combustion of fuel oils rich in sulphur do not cause corrosion at high temperatures. The author (Moore) has frequently run engines on oils containing over 3 per cent. of sulphur, and has never been able to note any effects on the engine parts which could be caused by this constituent. Exhaust pipes and silencers which are at comparatively low temperatures are sometimes affected by the sulphuric acid formed in the exhaust, but parts which are maintained at a temperature over 150° C.

TABLE XIII.

*Results showing calorific value, power developed in engine tests, specific gravity and percentage of sulphur in various typical gasolines from Mid-Continent and Eastern fields. (U.S. Bureau of Mines, Tech. Paper, No. 163.)*

| Sample number | Field from which sample was obtained | Process of manufacture | Gravity          |      | Calorific value of gasoline |                     | Power developed horse-power hours per pound of gasoline | Sulphur content per cent. |
|---------------|--------------------------------------|------------------------|------------------|------|-----------------------------|---------------------|---|---------------------------|
|               |                                      |                        | Specific gravity | °B.  | Calories per gram           | B.T.U. v. per pound |   |                           |
| 22            | Mid-Continent                        | Cracking plant         | .745             | 57.9 | 11,165                      | 20,097              | 1,345   | .02                       |
| 26            | "                                    | "Straight", refinery   | .742             | 58.7 | 11,174                      | 20,113              | 1,403   | .01                       |
| 43            | "                                    | "                      | .733             | 61.0 | 11,180                      | 20,124              | 1,350   | .05                       |
| 13            | Eastern                              | "                      | .718             | 65.0 | 11,187                      | 20,137              | 1,405   | .04                       |
| 19            | Mid-Continent                        | "                      | .724             | 63.4 | 11,215                      | 20,187              | 1,395   | .05                       |
| 38            | "                                    | "                      | .727             | 62.6 | 11,221                      | 20,198              | 1,396   | .03                       |
| 15            | Eastern                              | Blended casing head    | .733             | 61.0 | 11,230                      | 20,214              | 1,376   | .03                       |
| 1             | "                                    | "Straight", refinery   | .724             | 63.4 | 11,236                      | 20,225              | 1,420   | .03                       |
| 34            | Mid-Continent                        | "                      | .715             | 65.8 | 11,250                      | 20,250              | 1,365   | .02                       |
| 9             | Eastern                              | "                      | .687             | 73.8 | 11,315                      | 20,367              | 1,487   | .02                       |

do not allow the condensation of these acids, and are therefore not affected."

Blount<sup>1</sup> records sulphur content of petrol fuels on the market from 0.03 to 0.07 %.

It is thought that the question of sulphur in petroleum spirits does not justify further consideration from a fuel point of view and this contention is upheld by Graefe<sup>2</sup>.

### (h) Unsaturated hydrocarbons

Amongst the unsaturated hydrocarbons apparently there are to be found those bodies that are undesirable in petrol used as motor fuel<sup>3</sup>.

For this reason a quantitative measure of their presence is of commercial importance. Complete analysis as stated elsewhere being an operation of considerable difficulty the fairly rough methods that are available for these determinations suffice.

The methods are:

1. Sulphuric acid absorption.
2. Iodine absorption.

1. **Sulphuric acid absorption.** By this test a rough idea is given of the quantity of hydrocarbons in the spirit that could be taken out by further refining with sulphuric acid. It is of little value when applied to the straight run product since usually only a brown colouration results.

The method is simple, a small quantity, say 25 ccs. of the sample is agitated for five to ten minutes with

<sup>1</sup> *Inst. Automob. Eng.* III. p. 301, 1908-9.

<sup>2</sup> "Influence of sulphur in liquid fuel in internal combustion engines," *Diesel Engine Users Assocn.* 1915. See also Mollwo-Perkin, "Sulphur in Petroleum oils," *J. Inst. Pet. Tech.* III. 227, 1917.

<sup>3</sup> This, at any rate, is the view held to-day. The author firmly believes that within two or three years the above statement will require considerable modification.

an equal volume of sulphuric acid (sp. gr. 1.85). The liquids are then allowed to settle. The increase in volume of the sulphuric acid represents the material absorbed and this quantity multiplied by 4 gives the percentage absorption for the sample under test.

Although this test is sometimes stipulated in specifications it would be better to be guided by the following method of estimation.

2. **Iodine absorption.** It has already been pointed out that the higher percentage of unsaturated hydrocarbons in the 'cracked' and the shale spirits is shown by their greater iodine values.

The iodine value requires care in its estimation since local conditions of temperature, time of reaction, etc., readily influence the reactions on which it depends.

There are various methods in use for making this determination but the most satisfactory is that advocated by Messrs Rittman, Jacobs and Dean and described as follows<sup>1</sup>:

"A particularly satisfactory and sensitive method of differentiating gasolines with regard to their content of unsaturated hydrocarbons is the determination of iodine numbers. Iodine numbers, of course, represent only approximately the theoretical iodine absorption, as they are dependent on conditions of temperature and concentration and on the nature of the reaction. It is, therefore, necessary in giving iodine numbers to specify the conditions under which they were measured. For purposes of comparison, however, the determination of iodine numbers is of great advantage. The measurements can be made with ease and accuracy, and the differences for varying

<sup>1</sup> *U.S. Bureau of Mines, Tech. Paper, No. 163, p. 13.*

saturation percentages are great because the molecular weight of iodine is high and each unsaturated bond on the hydrocarbon absorbs two atoms.

A 30-minute absorption period is recommended, and the quantities of oil and iodine should be so adjusted that at the end of the reaction 70 to 90 % of the iodine remains unabsorbed.

The procedure may be outlined briefly as follows:

A quantity of gasoline, generally varying from 0.04 to 0.20 gram, was measured from a capillary pipette into an iodine absorption flask containing 10 cc. of chloroform or carbon tetrachloride. 10 cc. of Hanus solution, prepared by dissolving 13.2 grams of iodine and 3 cc. of bromide in a liter of glacial acetic acid, was added, and the flask was stoppered and set aside in the dark for 30 minutes. At the end of this time 25 cc. of 10 % potassium iodide solution was poured in and then 100 cc. of distilled water was added. The excess of iodine was determined by titration with sodium thiosulphate solution, prepared by dissolving about 25 grams of sodium thiosulphate to the liter and standardizing against iodine liberated by a standard potassium dichromate solution.

The iodine number is the percentage by weight of iodine absorbed. It is calculated by the following procedure: The titre of an unknown is subtracted from that of a blank (Hanus solution and chloroform or carbon tetrachloride allowed to stand 30 minutes without any gasoline) and the difference in cubic centimeters of thiosulphate solution is multiplied by the weight of iodine equivalent to each cubic centimeter of the solution. The weight of iodine thus found is divided by the weight of gasoline taken and multiplied by 100, giving the iodine number."

It is interesting to observe that the iodine value of petroleum products increases with an increase of boiling-point and specific gravity whereas with products from shale oil the reverse is the case, the lighter fractions showing the higher iodine value.

The iodine values and sulphuric acid absorption of several samples treated by this method, are given in the following table taken from the work of Messrs Rittman, Jacobs and Dean.

TABLE XIV.

*Iodine number and H<sub>2</sub>SO<sub>4</sub> absorption of typical American petrols.*

| Sample No. | State in which sample was obtained | Trade name of gasoline | Iodine No. | Percentage absorbed by sulphuric acid |
|------------|------------------------------------|------------------------|------------|---------------------------------------|
| 4          | Pennsylvania                       | "Motor" gasoline       | 7.9        | 1.0                                   |
| 17         | "                                  | 73° to 76° gasoline    | 8.4        | 2.2                                   |
| 21         | Indiana                            | 72° gasoline           | 8.5        | 2.0                                   |
| 23         | Louisiana                          | Gasoline               | 10.5       | 2.0                                   |
| 15         | Pennsylvania                       | "Motor" gasoline       | 13.4       | 1.6                                   |
| 7          | "                                  | "Auto" gasoline        | 14.9       | 2.6                                   |
| 25         | Louisiana                          | Gasoline               | 18.3       | 2.6                                   |
| 44         | Wyoming                            | "                      | 43.8       | 3.6                                   |
| 24         | Louisiana                          | "                      | 44.7       | 3.1                                   |
| 20         | Indiana                            | 62° naphtha            | 48.8       | 5.2                                   |
| 22         | "                                  | Gasoline               | 52.7       | 6.2                                   |

It is usual also to find recorded the bromine value of a petrol, this is readily converted to the iodine value by multiplying by the factor  $\frac{127}{80}$  the proportion of the atomic weights of bromine and iodine.

In the *Bureau of Mines Technical Paper*, No. 163, the following scheme of classification of gasolines is adopted.

1. Uncracked gasolines.
2. Blends with small percentage of cracked spirit.

### 3. Ordinary marketable cracked gasolines.

Class 1 gives iodine values of 6.5 or less.

Class 2 gives iodine values of 6.5 to 20.

Class 3 gives iodine values of 20 to 60.

#### (i) Aromatic hydrocarbons

The estimation of the aromatic hydrocarbons in petroleum spirit is of value in determining the possibility of extraction of such bodies as benzene, toluene, etc. Since the beginning of the war it has been necessary to investigate all the possible sources of toluene for the preparation of explosives.

It may here be mentioned that cracked spirits contain generally a greater percentage of aromatics than the straight-run spirits but that economically it is better to extract these bodies from the latter.

The rough method of estimation is by means of agitating the sample with nitrosulphuric acid and noting the absorption. The presence of benzene is indicated by the characteristic odour resembling bitter almonds.

For the accurate determination references should be made to a highly instructive paper of Bowrey<sup>1</sup> in which he describes a method where extraction is effected by sulphur dioxide at a low temperature followed by fractional distillation.

The qualitative method of Holde is described as follows. As much asphalt as will go on the end of a penknife finely powdered and free from inorganic material is put on a filter and the spirit to be examined is poured over it. If the filtrate is not coloured the absence of any considerable quantity of added benzol

<sup>1</sup> *Journ. Inst. Pet. Tech.* III. 287 (1917).

is confirmed, if the filtrate is yellow or brown in appearance, benzol or toluol are indicated.

The test depends upon the solubility of asphalt in these aromatic hydrocarbons and will detect 5 % to 10 % of benzol in petrol. The asphalt used for the test must have been washed previously with petroleum ether.

### (j) Acidity

The possible retention of traces of acid from the sulphuric acid treatment during refining is very improbable, nevertheless, it is frequently desirable that a test for acidity should be applied.

Acid is detected by agitating the spirit with warm water for a minute or two when the aqueous extract must not turn blue litmus paper pink; or alternatively, when 100 ccs. of the spirit are shaken with 10 ccs. of neutral distilled water and one drop of N/10 caustic soda is added the aqueous layer must not impart a pink colouration to phenol phthalein.

### (k) Purity

During its transport from the refinery to the consumer it is possible for the petrol to become contaminated with dirt or water. It is therefore necessary to look for these impurities when receiving any quantity of petroleum spirit.

The presence of suspended matter is immediately betrayed on visual inspection. Similarly, any dirt in the containers is readily detected.

Discolouration of the petrol would indicate the presence of some impurity dissolved in the spirit as for example the yellow to brown stain of mineral lubricating oil. The spirit should be water white.

Water is slightly soluble in petrol so that the ab-



sence of visible drops of water is no guarantee that it is entirely absent.

Groschuff has shown that the solubility is such that 100 grs. of benzine will dissolve 0.03 gr. water at 3° C., and 0.337 gr. water at 77° C.

Therefore, although water is not likely to be present in very considerable quantities it is usual to reduce the temperature of a sample to well below zero Centigrade when its presence is shown by a cloudiness due to the formation of minute ice crystals.

A point of interest in this connection was recently brought to the notice of the writer. In the investigation of a certain dyestuff it was found that it was completely insoluble in pure petrol but that the slightest trace of water in the petrol rendered it a solvent for the dye. A dye, such as, for example 'Sudan' which imparts a pink colouration to the petrol in which it is dissolved, is sometimes used for denaturing for Customs and Excise purposes. Thus in Roumania to encourage the use of benzine for industrial power, it is sold in the country at prices considerably below export figures and to guard against possible fraud it must be denatured in the above manner.

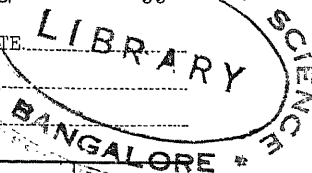
The presence of any 'dopes' in petrol is not likely to be detected in samples of the usual brands on the market but it may be mentioned that the presence of picric acid would be shown by the deposition of crystals of that substance on evaporation of the spirit, or by the yellow colouration imparted to a small quantity of water shaken with the suspected sample.

A copy of a typical laboratory report form for petrol is here inserted (Fig. 26) to show the information usually called for in routine testing.

PETROL CERT. No. ....

DATE .....

SAMPLE SUBMITTED BY .....



|                                       |      |      |      |      |      |
|---------------------------------------|------|------|------|------|------|
| Laboratory No.                        |      |      |      |      |      |
| Marks on Label removed from Tin.      |      |      |      |      |      |
| D. 15                                 |      |      |      |      |      |
| I. B. P                               |      |      |      |      |      |
| at 50° C.                             |      |      |      |      |      |
| at 60° C.                             |      |      |      |      |      |
| at 70° C.                             |      |      |      |      |      |
| at 80° C.                             |      |      |      |      |      |
| at 90° C.                             |      |      |      |      |      |
| at 100° C.                            |      |      |      |      |      |
| at 110° C.                            |      |      |      |      |      |
| at 120° C.                            |      |      |      |      |      |
| at 130° C.                            |      |      |      |      |      |
| at 140° C.                            |      |      |      |      |      |
| at 150° C.                            |      |      |      |      |      |
| Flask Dry at °C.                      |      |      |      |      |      |
| At Temperature at which Flask is Dry. |      |      |      |      |      |
| Residue.                              |      |      |      |      |      |
| Loss.                                 |      |      |      |      |      |
| Total.                                | 100% | 100% | 100% | 100% | 100% |
| Colour.                               |      |      |      |      |      |
| Odour.                                |      |      |      |      |      |
| Water.                                |      |      |      |      |      |
| Suspended Matter.                     |      |      |      |      |      |
| Colour. Free                          |      |      |      |      |      |
| Defining Colour                       |      |      |      |      |      |
| Further Remarks.                      |      |      |      |      |      |

Fig. 26. Typical petrol certificate.

## B. FURTHER PROPERTIES

Further properties which have not been considered above, since they do not form the bases of routine testing, are the following:

### (a) Flash point

The flash point of an oil is expressed as that temperature at which the oil gives off vapour in sufficient quantity to cause a momentary flash on the application of a test flame. On further increase of temperature a point is reached where the oil burns continuously, this is known as the 'burning point' of the oil in question.

It will be realised, then, that the flash and burning points of petrol are considerably below the normal atmospheric temperature.

For lamp oils this determination is of value from the point of view of safety in storage and use.

For petrol the test results are more of interest than use.

The Abel-Pensky apparatus employed for flash point determinations is very fully described by Redwood<sup>1</sup> and others.

The results of tests on several petrol fractions are given below:

TABLE XV.  
*Flash points of petrol samples.*

| Boiling limits of sample | 50-60° | 60-78° | 70-88° | 80-100° | 80-115° | 100-150° |
|--------------------------|--------|--------|--------|---------|---------|----------|
| Flash point under        | -58°   | -39°   | -45°   | -22°    | -21°    | +10°     |
| Burning point            | -      | -34°   | -42°   | -       | -19°    | +16°     |

<sup>1</sup> II. 215.

It is understood that these determinations are made at normal atmospheric pressure for any change in the pressure will influence the flash point.

Tables for correction for barometric pressure are supplied with the instrument.

### (b) Explosibility

The dangerous nature of its vapour is perhaps the most characteristic property of petrol.

Petrol is always inflammable at atmospheric temperatures as is indicated by its very low flash point, but it is explosible only when certain proportions of its vapour are mixed with the air.

The safe limiting values of those proportions are 2.3 % and 5 %. Thus one pint of petrol will on evaporation render 100 cubic feet of air highly explosive but very much more or less than that one pint will not have the same effect.

The normal range of explosibility is shown in the following table (XVI) where comparison is drawn with other substances.

Experiments<sup>1</sup> made under various conditions of ignition and size of gas container have shown the limits of explosibility to be between 1.4 and 6.4 %. On increasing the initial temperature of the vapour the percentage of petrol forming an explosive mixture is reduced, thus, at 400° C. the lower limit is between 1.02 and 1.22 %.

The explosive range is of particular interest to internal combustion engineers to whom the wider range in the case of alternative fuels appeals as an advantage over petrol.

<sup>1</sup> Burrell and Boyd, *U.S. Bureau of Mines, Tech. Paper*, No. 115.

TABLE XVI.

*Explosive limits of various vapours.*

| Kind of vapour   | Percentage of inflammable vapour in mixture |           |              |
|------------------|---|-----------|--------------|
|                  | No explosion                                | Explosion | No explosion |
| Water gas        | 12.3  | 12.5-66.6 | 66.9         |
| Illuminating gas | 7.8   | 8-19      | 19.2         |
| Benzol           | 2.6   | 2.7-6.3   | 6.7          |
| Pentane          | 2.3   | 2.5-4.8   | 5.0          |
| Petrol           | 2.3   | 2.5-4.8   | 5.0          |

With a wide range of explosibility, engine trouble and consequent stoppage due to the misfiring of non-explosive mixtures are rendered less probable.

### (c) Spontaneous ignition temperature

The spontaneous ignition temperature of a fuel may be defined as that temperature at which the fuel will ignite in air or oxygen without the application of a flame or spark.

This value from a fuel point of view is useful for calculations in connection with internal combustion engines.

For its determination reference should be made to Moore<sup>1</sup> whose apparatus and information are both ingenious and instructive.

Moore's results show that for petrol this value is relatively constant, varying in four typical samples as below:

<sup>1</sup> Moore, *Liquid Fuels for Internal Combustion Engines*, 1918 (Crosby Lockwood).

TABLE XVII.

*Spontaneous ignition temperatures.*

| Sample          | Sp. gr. | Spont. ignit.<br>temp. in oxygen | Spont. ignit.<br>temp. in air |
|-----------------|---------|----------------------------------|-------------------------------|
| Pratt's No. 1   | 0.710   | 272° C.                          | 383° C.                       |
| Mex             | 0.718   | 279                              | 361                           |
| Pratt's No. 2   | 0.724   | 270                              | 371                           |
| Taxibus (Anglo) | 0.729   | 272                              | 390                           |

The value varies with different pressures but a comparison may be drawn between one fuel and another at any temperature. A high temperature of spontaneous ignition is of advantage in the automobile and aero-engine as it would indicate a lesser liability to pre-ignition.

*(d) Specific heat*

This property may be defined as the quantity of heat in calories required to raise the temperature of one gram of any substance through one degree Centigrade.

The specific heat capacity, or coefficient of thermal capacity as it is alternatively termed, varies directly with the hydrogen content of the oil, thus of two oils, that one containing the higher proportion of hydrogen will have the higher specific heat capacity.

The value of the specific heat is confined to calculations relating to the design of rectifiers, etc.

Gracfe gives a value for American naphtha as 0.487 calories.

Other figures recorded are:

|                    |             |        |
|--------------------|-------------|--------|
| Petroleum ether at | — 190° C.   | 0.452, |
| „                  | „ — 100° C. | 0.445, |
| „                  | „ 0° C.     | 0.419. |

(e) **Heat of vaporization**

This is defined as the quantity of heat required to convert one kilogram of a substance at its boiling-point to vapour at the same temperature.

The following values are given:

TABLE XVIII.  
*Heats of vaporization.*

|                       | B.P.   | Heat of vaporization |
|-----------------------|--------|----------------------|
| Hexane                | 69° C. | 79.4 calories        |
| Heptane               | 98     | 74.0    "            |
| Octane                | 125.5  | 71.1    "            |
| Decane                | 173    | 61.0    "            |
| Heavy benzine (0.743) | 91-95  | 79.6    "            |
| Benzol                | —      | 100    "             |
| Alcohol               | —      | 200    "             |

This figure is of use in heat calculations connected with the condensing plant of refineries. On cooling vapours the heat of vaporization or latent heat is surrendered when they attain the liquid state and it is of interest to know how much heat is thus given up or must therefore be removed from a given volume of vapour. The figure is valuable also to the designer of carburetters.

(f) **Optical properties**

The optical properties of petroleum products are of value in some cases as a means of detecting them in mixtures with or as adulterants in other oils. In the case of petrol, however, the optical properties have no immediate interest in technical examination.

It is possible that the optical properties combined

with the results of other tests may give some indication of the origin of a petrol<sup>1</sup>.

The following values for the refractive index of various petrols are given.

TABLE XIX.

*Specific gravity and refractive index.*

| Source      | Specific gravity | Refractive index |
|-------------|------------------|------------------|
| Pechelbronn | 0.7550           | 1.4210           |
| Oelheim     | 0.7830           | 1.4350           |
| Baku        | 0.7820           | 1.4360           |
| American    | 0.720            | 1.3995           |
| Russian     | 0.720            | 1.4105           |
| Roumanian   | 0.720            | 1.4005           |

The following table after Chercheffsky<sup>1</sup> shows the indices of refraction for several spirits as functions of their specific gravities and their boiling points.

TABLE XX.

*B.P. limits and refractive index.*

| Origin           | Sp. gr.<br>at 15° C. | Mean of<br>B.P. limits | Index of<br>refraction<br>at 15° C. | Mean of<br>B.P.<br>limits | Sp. gr.<br>at 15° C. | Index of<br>refraction<br>at 15° C. |
|------------------|----------------------|------------------------|-------------------------------------|---------------------------|----------------------|-------------------------------------|
| American         | 0.780                | 191° C.                | 1.4345                              | 150° C.                   | 0.754                | 1.4203                              |
| Russian          | 0.780                | 158.5                  | 1.4309                              | 150                       | 0.775                | 1.4282                              |
| Roumanian        | 0.780                | 153                    | 1.4334                              | 150                       | 0.7785               | 1.4324                              |
| Galician         | 0.780                | 166                    | 1.4356                              | 150                       | 0.7665               | 1.4278                              |
| Shale<br>naphtha | 0.780                | 167.5                  | 1.4373                              | 150                       | 0.766                | 1.4302                              |

Petrols have practically no optical rotatory power, thus they are readily distinguished from turpentine for which they are used as substitutes.

<sup>1</sup> *Comptes Rendus*, 150, 1338-41, 1910, Chercheffsky.



## (g) Solubility in alcohol

Normal petrol is completely soluble in absolute alcohol but not so with a diluted alcohol, e.g., 90 %.

Blackler<sup>1</sup> has stated that when a cracked spirit, of boiling-points from 35° C. to 220° C., mixed with equal quantity of alcohol, was distilled, 90 % of distillate was collected below 100° C.

The question of the depression of boiling point in such mixtures is taken into account in the consideration of mixed fuels.

## (h) Congealing point

One of the advantages, from the point of view of a fuel for aero-engines, possessed by petrol is that its point of congelation is considerably below the coldest temperatures experienced in the atmosphere.

Petrol solidifies below - 160° C.

The following figures show the results of tests on various petrols for the determination of the rate of solidification at - 190° C.

TABLE XXI.  
*Rate of congelation at - 190° C.*

| Description | Sp. gr.<br>at 15° C. | Engler distillation percentage volume<br>100 ccs. |           |                   |                    | Time in<br>secs. to con-<br>geal from<br>laboratory<br>temp. to<br>- 190° C. |
|-------------|----------------------|---|-----------|-------------------|--------------------|--|
|             |                      | - 69° C.  | 69°-98°·5 | 98°·5 -<br>125°·5 | 125°·5 -<br>149°·5 |  |
| German      | 0·710                | 40  | 57        | 1                 | nil                | 29·6   |
| Pratt's     | 0·718                | 3   | 77        | 18                | nil                | 22   |
| Shell A     | 0·725                | 13  | 57        | 25                | 3                  | 21·5   |
| Mex         | 0·725                | 2   | 48        | 38                | 10                 | 10·5   |
| Shell A     | 0·732                | 7   | 42        | 34                | 15                 | 10·2   |

<sup>1</sup> *Journ. Inst. Pet. Tech.* III, 115.

The state of the petrol in the above case is its solid condition physically. Many attempts have been made to solidify petrol for convenience (?) in transport and safety in storage. Rosculetz has patented a process by which petrol is converted by the addition of harmless substances into a jelly resembling in appearance Brand's essence of beef. Other processes employing admixed stearine as an ingredient, have attained partial success but, on the whole, no great advantage appears to be derived from the attainment.

### (i) Physiological

Apart from the asphyxiating effects of petroleum vapours upon workmen in the petroleum refineries, the finished products are known to have an irritating action on the human skin. Although many workers appear to be immune from this action, it is usual after handling oils with bare hands to wash the skin free of any oil.

In places where petrol is used as a solvent and the vapours are able to spread through the workrooms it is necessary to provide efficient ventilation to avoid pollution of the air.

Some of the lightest varieties of petroleum spirit are used as local anaesthetics.

## CHAPTER VI

### USES

#### (a) General

THE use of petrol as the source of energy for the motor car is known to everyone, but many of the other purposes for which the light petroleum distillates may be used are by no means familiar.

Perhaps the quaintest service rendered by petroleum spirit is as a lubricant in liquid air machines, this because of its very low congealing point.

Further uses, beyond that of fuel, are as illuminant, anaesthetic, solvent and as the raw material for the extraction of aromatic hydrocarbons, benzene, toluene, etc., for the preparation of dye-stuffs, explosives and drugs.

The varieties of spirits obtainable from petroleum may be judged from the foregoing description of their preparation.

These innumerable varieties are described by a large number of terms that are unfortunately very loosely applied; consequently products known under one name may vary quite considerably if prepared or bought under different circumstances.

In the following list, therefore, no claim can be made for accurate definition, and the descriptions must be regarded as only approximate.

Many of the names are given, it would appear, as the results of some particular use to which the spirit is put rather than on the properties it possesses.

TABLE XXII.

*Trade and other names for petroleum spirits.*

|   |   |   |
|---|---|---|
| Cymogene (B.P. 0° C. sp. gr. 0.583, gas at ordinary temperatures) | The lightest varieties of petroleum spirits with specific gravities from 0.583 to 0.700 | Used as anaesthetics, solvents, etc., also for carburetting air for petrol-air gas            |
| Canadol   |   |   |
| Rhigolene (B.P. 18° C., sp. gr. 0.600)                            | Cymogene (practically butane) condensed from gas coming off before distillation begins  |   |
| Sherwood oil (sp. gr. 0.650 to 0.666, B.P. 70°-90°)               |   |   |
| Petroleum ether   | Heavier than above with sp. gr. of 0.700 to 0.730                                       | Used as fuel for light cars and aircraft, solvents, oil extraction, etc.                      |
| Keresoline  |   |   |
| Benzoline   | Heaviest fractions of petroleum spirits with sp. gr. of 0.730 to 0.765                  | Used as fuel for benzine motors and heavy vehicles and (up to 0.800) as turpentine substitute |
| Danforth oil  |   |   |
| Ligroin   |   |   |
| Boulevard gas fluid   |   |   |
| Normal benzine  |   |   |
| Benzine (light)   |   |   |
| Petrol  |   |   |
| Gasoline  |   |   |
| Naphtha (heavy)   |   |   |

The limits of boiling-point and other properties of the above-mentioned products vary with the nature of their application.

Trade terms for petroleum spirits include also, Carburine, Movril, Taxibus Spirit, Shell Spirit, Pratt's and Swan Spirit.

The types of petroleum spirits employed for several purposes are described in the following remarks.

#### (b) Solvent

For this purpose petroleum spirits are used in chemical laboratories and chemical industries such as those dealing with rubber, varnishes, explosives, dry-cleaning, linoleum and oil-extraction.

Petroleum ether used in chemical laboratories is composed chiefly of paraffin hydrocarbons with boiling-points from 35° C. to 50° C. (i.e., chiefly pentane). The presence of small amounts of unsaturated hydrocarbons appears to give no trouble in its use as a solvent.

Ligroin is a heavier variety of above with higher boiling-points.

Normal benzine used for the testing of asphalt in mineral oils has a specific gravity of 0.695 to 0.705 and boiling-point limits of 65° C. to 95° C. The sulphuric acid absorption for unsaturated and aromatic hydrocarbons should show no more than 2 % soluble in the concentrated and fuming sulphuric acid.

Petroleum spirits are used in the varnish industry for their high volatility. The specific gravity varies from 0.690 to 0.700 but sometimes lighter spirit is required.

The solvent should not contain those high boiling-point residues known as 'naphtha bottoms' or 'kerosene tails.'

As an example of the relative volatility of various solvents the following figures are quoted.

TABLE XXIII.  
*Rate of evaporation of solvents.*

|                          |            |
|--------------------------|------------|
| Benzol (90 %)            | 14 minutes |
| Commercial toluol        | 33 "       |
| Solvent naphtha          | 107 "      |
| Turpentine               | 142 "      |
| Petroleum spirit (0.666) | 4 "        |
| " " (0.700)              | 8 "        |

The above figures<sup>1</sup> are obtained by evaporating 2 ccs. of the substance from a metal surface 3½ inches square.

<sup>1</sup> North, *J. Ind. Eng. Chem.*, Nov. 1917.

The lighter solvent spirits are used also in the manufacture of rubber cements and the heavier varieties for paint mixing.

'Solvent naphtha' it should be noted is not a petroleum product but a distillate of wood or coal tar. 'Green naphtha' is another term for shale spirit.

The extraction of oil from seeds is frequently effected by means of petroleum spirit. Castor oil, for example, is practically insoluble in petrol at low temperatures but is soluble in hot spirit.

The spirit used for this purpose should be well refined and sweet in odour. It should have a boiling range as narrow as possible and contain no kerosene tails. The fractions should be as free as possible from dissolved gas. The lower boiling-point should be near  $100^{\circ}\text{C}$ . so that the material will be already at that temperature when extraction is begun, otherwise water might condense and cause the extracted mass to become pasty<sup>1</sup>.

The solvent properties of benzine are turned to account in dry-cleaning<sup>2</sup>, or, *nettoyage à sec*.

In the dry-cleaning process the benzine dissolves out the fatty substances and grease to which adhere the particles of dirt and dust that render a garment soiled.

Originally, light petroleum spirits of specific gravity of about 0.700 were used for this purpose (other solvents being benzol and carbon tetrachloride) but of recent years heavier gravity, up to 0.780, benzine has been employed.

A particularly volatile spirit will result in heavy evaporation losses and, conversely, a spirit containing

<sup>1</sup> Ubbelohde, i. 606.

<sup>2</sup> Farrell, *Dyeing and Cleaning*. Griffin.

too great a proportion of high boiling-point fractions, will not evaporate sufficiently quickly after use; thus, it is considered that the most suitable spirits are those with boiling-points of 80° C.-120° C.

It is naturally essential that the solvent should have no unpleasant odour and for this reason well refined benzine is sought.

An interesting point to be observed in the use of benzine in dry-cleaning machinery is the liability of the spirit to ignition as a result of the generation of frictional electricity from the moving parts.

Any difference of potential set up by the friction of the machines and the clothes contained, may cause a sparking which, in a dry atmosphere, would result most probably in fire.

To obviate this danger it is usual to 'earth' most carefully any conductors in the plant.

A further means of lessening this liability is by adding a substance which will render the spirit a conductor of electricity.

Such a substance is, for example, magnesium oleate, when added in the proportion of 0.02 %-0.05 % of the mass of spirit to be treated. In some parts of the dry-cleaning process, however, it is not practicable to work with this soap.

A further caution against sparking has been suggested recently in the case of the common practice of filtering petrol through chamois leather before use. It is advised that the filter should be arranged in metallic contact with the container receiving the filtrate and thus to earth, or, better, to employ only wire gauze filters.

The soiled spirit from the dry-cleaning process is recovered by distillation in small steam-heated stills

and where necessary it is refined with sulphuric acid followed by soda or water washing.

### (c) Illuminant

For the purposes of lighting in country houses, etc., far removed from usual gas and electricity supplies, petrol air-gas plants are sometimes conveniently installed.

In petrol air-gas or gasoline-gas a mixture is made, of petrol vapours with air, that will serve as a combustible gas, giving, as the result of its combustion, either a luminous flame or a non-luminous flame sufficiently hot to raise the temperature of an incandescent mantle to white heat.

A rich gas will require about 4 or 5 gallons of benzine, per 1000 cubic feet of air, this will burn in an ordinary flat-flame burner.

With rich gases, however, there is always a danger, for, although they are in themselves not explosible there remains the liability of escape into the atmosphere of a room where, with the requisite quantity of air, they may become highly explosive.

With poorer gases the case is different, they contain too small a percentage of vapour (1.5–2 %) to be dangerous and on escape can only become diluted. These latter can be used only as heating gases so that for lighting purposes incandescent mantles have to be introduced.

As in many of the other applications of petrol, the quality of spirit used has varied from very light distillates, e.g., 0.680 to 0.700, that were the commercial products of yesterday, to the heavier grades that are now on the market. The quality of petrol used for petrol air-gas is similar to that used as light motor



fuel, therefore, given the desirable volatility, the heavier gravity spirit, purchased by the gallon, will be more economical from the point of view of heat units obtainable from it.

A modification of the use of air carburetted with petrol is found in the 'petrolite lamp.'

'Petrolite' lamps are fed on light spirit of a highly volatile nature, usually branded on the market as 0.680 specific gravity.

The following description of the lamp is taken from a pamphlet of the vendors (The Petrolite Safety Lamp Co.):

"The container consists of a highly absorbent and incombustible stone. This stone, which is perforated to allow for the passage of air, is placed in the container and filled with petrol, which is immediately absorbed by the stone. There is thus no free liquid in the lamp, and explosion is rendered quite out of the question, as the petrol once absorbed in the container becomes more harmless than ordinary air, as it is impossible to get it out again from the stone in liquid form. It 'swallows' the petrol only to give it up again as vapour, and this very slowly indeed, by suction.

The action of the lamp may be shortly described as follows: The insertion of a lighted match in the opening of the burner gallery causes immediately a slight draught in the chimney, sufficient to produce a suction in the inner burner tube. The cold air thus drawn into the lamp has to make its way through the perforations of the stone saturated with petrol. During this passage the air is being carburetted with vapour, and this diluted gas, while being drawn up the burner tube, meets on its way with a further

supply of cold air from the outside. Both are automatically mixed in the exact proportion to give a very hot Bunsen flame with perfect combustion.

It will thus be clearly seen that the evaporation of the petrol in the lamp is not produced by heat, as is almost invariably the case with the other lamps (certainly a wrong and most dangerous method), but by causing a draught of cold air to pass through the Petrolite container. In this way the burner produces a sufficiently hot Bunsen flame for the most brilliant incandescent light, while the temperature of the lamp body is lower than that of the surrounding air, thus eliminating one of the many sources of danger in other lamps."

#### (d) Fuel

It is as fuel that the demand for petrol has risen so rapidly. The increased use of motor traction has converted petrol from a despised, dangerous spirit to little less than an everyday commodity.

The value of petrol as fuel in the internal combustion engine has been demonstrated in the present war where whole armies of transport, fleets of aircraft and, more recently, tanks, have been driven on petrol.

In the first instance only the lightest spirits were employed as fuel, but with the improvement in engine design of recent years it has been found possible to employ a much larger range of products than hitherto.

Speaking generally, the lighter spirits are used for the lighter engines and heavier engines are run, apart from entirely different fuels, on distillates approaching the kerosene fractions.

It will be interesting to record several specifications for petrol fuel bearing in mind that they can possess only temporary value since they must be influenced

not only by the limited possibilities of supply but also by the engine improvements that permit of the use of higher boiling-point products.

It may be well to remember that the specific gravity of a spirit is a guide to quality, only when the source and other properties are known, so that to the refinery chemist in Pennsylvania a gasoline of 65° Bé has a definite meaning, but petrols on the market of 0·720 specific gravity will vary in their properties according to source and method of preparation. Specific gravity is therefore rapidly losing favour as a criterion of quality and other tests are required in the specifications.

Thus, Holde gives a specification for automobile benzine: it should be obtained by fractional distillation from petroleum, free from water and all substances likely to injure the motors. A filter paper moistened with the spirit should not show spots or give a persisting odour. It should be of uniform composition and not a mixture of high and low boiling products.

Again, light naphtha should distil 80 % under 100° C. and all under 130° C. Heavy naphtha 50 % under 100° C. and all under 140° C. The spirit must be carefully purified, have no colour and only a faint odour. Naphtha for passenger service should have a specific gravity of 0·700–0·720 at 15° C. and for commercial lorries 0·720–0·750.

The German Automobile Club specify for pleasure cars petrol of 0·685–0·700 and for commercial vehicles 0·705–0·720. It is stated that heavier oils cause fouling, irregular ignition and corrosion. Fractions boiling over 150° C. cause fouling of the cylinders.

The above views with regard to specific gravity are rapidly becoming superseded.

In a recently published Bulletin of the U.S. Bureau of Mines the essentially desirable properties of motor spirit are summarized as follows:

1. The gasoline should not contain too large a percentage of highly volatile products which tend to cause large evaporation losses and excessive danger in handling and storage, but should have sufficient volatile constituents to permit starting an engine under reasonably unfavourable conditions without preheating.

2. The gasoline should not contain any considerable percentages of heavy or non-volatile constituents which, after atomisation into the engine cylinders, cannot be completely vaporised and burned.

3. The gasoline should not contain a material which after combustion leaves a residue that collects in the motor.

4. The gasoline should be free from substances that attack metal either before or after combustion; unremoved acid (used in refining) falls under this head.

5. Neither the gasoline nor its products of combustion should have a strong or markedly disagreeable odour because of this being objectionable to users of automobiles.

6. The gasoline should be free from non-combustible material, such as water, sediment, acid, etc.

After a consideration of the various factors influencing the quality the following specifications for motor spirit are suggested:

“COLOUR: *Requirement.* Water white.

*Method of determination.* Inspection of column in 4-ounce sample bottle.

ACIDITY: *Requirement.* Total absence.

*Method of determination.* 10 cc. of the gasoline is

to be shaken thoroughly with 5 cc. of distilled water. The aqueous extract must not colour blue litmus paper pink.

**VOLATILITY: Requirements.** The gasoline shall, when distilled by the method described hereafter, meet the following requirements:

(a) The temperature read on the thermometer when 20 per cent. has distilled shall not be below 70° C. (158° F.) nor above whatever limit is fixed after due consideration of conditions of use.

(b) The temperature read when 90 per cent. has distilled shall not be above another limit similarly chosen.

(c) The temperature read when 50 per cent. has distilled shall not be higher than a mark half-way between the 20 per cent. and the 90 per cent. limit.

(d) The dry point shall not exceed the actual 90 per cent. reading by more than 55° C. (99° F.).

**Tolerance.** If either the 20 per cent. or the 90 per cent. temperature mark is above the required limit by an amount not exceeding 10° C. (18° F.), the gasoline may be considered acceptable if the sum of the two temperatures read for the 20 and the 90 per cent. marks do not exceed the sum of the adopted limits."

The method of distillation is that described on p. 74.

The following classification has been recently proposed:

TABLE XXIV.

*Proposed classification of petrol fuels (American).*

| Volume distillate | " 130 " | " 155 " | " 180 " |
|-------------------|---------|---------|---------|
| 20 % not below    | 50° C.  | 50° C.  | 50° C.  |
| 20 % not above    | 75      | 90      | 105     |
| 60 % "            | 100     | 120     | 140     |
| 90 % "            | 130     | 155     | 180     |
| Dry point         | 165     | 190     | 215     |

The "130" spirit is suggested for aircraft and the "155" and "180" for use in light and heavy engines respectively.

Mr E. Lawson Lomax<sup>1</sup> has submitted the following gradings for motor spirit by his method of testing which has been referred to on p. 70.

TABLE XXV.

*Proposed classification of petrol fuels (Lomax).*

|                        | No. 1 Quality | No. 2 Quality | Taxibus and Heavy Motor Quality |
|------------------------|---------------|---------------|---------------------------------|
| Volatile below 100° C. | 25-30 %       | 15-25 %       | 10-15 %                         |
| "      "      125      | 60-65         | 50-60         | 45-50                           |
| "      "      150      | 85-90         | 70-80         | 60-70                           |
| Final boiling point    | 170°-180° C.  | 190°-200° C.  | 200°-210° C.                    |

The desirable features in a petroleum spirit to be used as a motor fuel will now be discussed.

It has been shown that the question of specific gravity is one of only secondary importance and that within very wide limits it can have no influence on the quality of fuel.

Calorific value, similarly, need hardly be considered since it is roughly the same for all petrols and, when it is remembered that the average thermal efficiency of the petrol motor is under 25 %, the difference between a high and low calorific value (of petrol) is negligible. Given the requisite engine conditions all petroleum spirits will develop the same amount of power.

General purity, that is, freedom from water or other contaminations, absence of acid traces, etc., are essentials of primary importance.

<sup>1</sup> *J. Inst. Pet. Tech.* iv. 1917.

A sufficient quantity of low boiling products to ensure easy starting of engines is essential and for the lighter type of engine the minimum of high boiling fractions is desirable.

As has already been stated, the question of chemical composition will possibly attract more attention in the future but for the time being this is of minor importance, particularly in the case of "straight-run" or blended casing-head gasoline.

With cracked spirits, however, the case is different. These, as has been stated, contain large quantities of unsaturated hydrocarbons, some of which may bring about during storage or use a polymerisation which results in the formation of gummy substances. This phenomenon forms the chief argument against the use, as fuel, of cracked spirits and shale naphthas.

It should be pointed out that these spirits have already received a very extended application in America and elsewhere and that no complaints have been heard as to their damaging effects in engines. From this fact alone it may be assumed that the commercial cracked spirits now produced are entirely satisfactory for fuel purposes, at any rate when consumed soon after manufacture.

Nevertheless, it would be inadvisable, until we know more of the chemical composition of these substances and the precise nature of those compounds that are the cause of the gummy deposits, to accept cracked spirits as general substitutes for normal petrol when the possibility of long storage must be considered.

Investigations are being carried out at the present time to discover exactly what are the undesired constituents in the less satisfactory of the cracked

spirits; whether these can be converted by processes of hydrogenation into products more closely resembling those found in straight-run petrol, or whether more careful refining with various reagents and methods can eliminate them altogether from the finished products.

In conclusion, since many spirits which contain appreciable quantities of these unsaturated bodies have been on the market and in general use for some years without complaint, it may be assumed that the dangers of using cracked spirit have been grossly exaggerated. On the other hand it must be borne in mind that there are some unsaturated bodies that are distinctly harmful and until the chemical nature of these substances and the precise means of their transformation or elimination are definitely ascertained there is every justification for regarding cracked spirits at least with caution for work where the very greatest care in the selection of a liquid fuel is essential.

The question of sulphur content in petrol and its effect in use of the spirit as fuel has been referred to under the examination of petrol for sulphur. The views recently expressed by Moore are entirely concurred in by the present writer. It should be pointed out that complaints have frequently been made that in petrol tanks, at points where it is possible for electrolytic action to be set up, corrosion has been observed and attributed to the presence of sulphur in the fuel. No experimental data, beyond the familiar discolouration of brass by kerosene, are given to show to what degree this contention may be correct, and under these circumstances the author prefers to remain agnostic.



(e) **Petrol dopes and substitutes**

There is a very definite line of division to be drawn between the genuine fuels that may be used in the internal combustion engine in place of petrol (such as, for example, benzol-alcohol mixtures<sup>1</sup>) and the so-called petrol 'dopes' and 'substitutes' the ingredients of which are frequently wrapped in mystery.

With the extended use of motor vehicles which will be brought about by the cheapening of the automobile and the possible future establishment of a peacetime fleet of commercial aircraft the consumption of light liquid fuel will reach a figure probably exceeding the world's output of petroleum spirit. It is only natural and desirable that other liquid fuels such as benzol and alcohol will attract more attention as such than hitherto.

On the other hand it is well to observe that as the result of developments in engine construction it is highly probable that in the future much heavier fractions of petroleum will be serviceable as fuel. The refiner will be able to make his 'cuts' further on in the crude oil distillation than in the past.

There will be a higher final boiling-point in the finished fuel which means that the kerosene yield of petroleum will be sacrificed to boost up the production of the petrol for liquid fuel. This is the appearance of things to-day.

When, however, we come to consider the 'dopes' we find an entirely different proposition. A cursory

<sup>1</sup> Watson, "Benzol, Alcohol and mixtures of these liquids with Petrol as fuels for internal combustion engines," *Proc. Inst. Autom. Eng.* p. 73, 1914.

glance at the patents of the last decade shows the number of efforts that has been made to obviate the difficulties experienced in using the kerosene fraction as liquid fuel for the lighter class of engines. These difficulties, such as starting trouble and fouling of cylinders due respectively to lack of sufficient volatile fractions and presence of higher boiling-point products, it is contended by the patentees, are overcome by the addition to the oil of various substances such as picric acid, a solution of white phosphorus in carbon disulphide, or acetone.

The artificial preparation of a mixture of substances to obtain a more useful fuel is certainly worthy of serious attention and it is the general belief that probably by this means a more economical use could be made of the liquid fuels at our disposal, but the claims put forward for some of the 'dopes' are not only based on unsound premises savouring of alchemical speculation but are obviously intended to deceive the purchaser and for this reason they justify the very strongest condemnation.

#### (f) Distribution

The greater part of the petroleum spirits imported to this country comes from America and the Dutch East Indies, supplied by the Standard Oil Company and the Royal Dutch Company respectively. These concerns obtain their supplies from various parts of the world but the bulk of their deliveries is derived from the above mentioned sources. Smaller supplies have been secured directly or indirectly from Mexico, Roumania and Persia.

The spirits are shipped to England in tank steamers which discharge at Portishead, near Bristol, Thames Haven, Barrow-in-Furness and other suitable ports. A number of storage tanks of large capacity is available at these places for the spirits.

From these stations the products are transported in railway tank-cars, which hold from 2,600 to 4,000 gallons, to the inland depôts of the distributing concerns.

Here, the spirits are filled into smaller containers such as 50 gallon drums or 2 gallon cans suitable for dispatch to works or to retailers.

Various precautions are taken during these periods of transport to reduce the possibilities of contamination to a minimum; thus, for example, when discharging a railway tank-car it is usual to test for the presence of water by inserting a long rod, one end of which is coated for a few inches with a "sugar" which is soluble in water but not so in petrol. If any of the "sugar" is dissolved from the end of the rod necessary action is taken.

It is the general practice in all storage tanks that are not built on brickwork or cement foundations to allow a small quantity of water to remain permanently at the bottom of the reservoir, this is done as a precaution against leakage which, in tanks, standing directly on or buried in, the earth, would not be detected. At the inland depôts the filling of 2 gallon cans is effected by automatic fillers checked in their quantity deliveries periodically by representatives of the Board of Trade.

Bulk deliveries to large consumers is made by railway tank-cars direct from the ocean stations.

*Accounts relating to Trade and Navigation*, Jan. 1918, gives the following figures for imports of motor spirit.

|      | Month ending 31st January |            |
|------|---------------------------|------------|
|      | Gallons                   | Value in £ |
| 1916 | 6,985,279                 | 275,015    |
| 1917 | 13,001,740                | 933,014    |
| 1918 | 15,335,570                | 1,172,472  |

The total imports of petroleum<sup>1</sup> for two years are as follows:

|      |                     |
|------|---------------------|
| 1915 | 588,469,699 gallons |
| 1916 | 451,556,152 „       |

<sup>1</sup> "Mines and Quarries: output," *H.M. Ch. Insp. Mines*, 1917.

## BIBLIOGRAPHY.

- Bacon and Hamor. American Petroleum Industry. McGraw Hill.  
 Beeby-Thompson. Oilfield Development. Crosby-Lockwood.  
 Brame. Fuel, Solid, Liquid and Gaseous. Arnold.  
 Clapp. Petroleum and natural gas resources of Canada. Department of  
 Mines, Canada.  
 Cooper-Key. Storage of Petroleum Spirit. Griffin.  
 Cunningham-Craig. Oil Finding. Arnold.  
 Farrell. Dyeing and Cleaning. Griffin.  
 Hager. Oil Geology. McGraw Hill.  
 Holde and Mueller. Examination of Hydrocarbon Oils. Wiley.  
 Johnson and Huntley. Principles of Oil and Gas Production. Chapman  
 and Hall.  
 Lewes. Liquid and Gaseous Fuels. Constable.  
 Lewes. Oil Fuel. Collins.  
 Moore. Liquid fuels for internal combustion engines. Crosby-Lockwood.  
 O'Connor. Petrol Air-Gas. Crosby-Lockwood.  
 Redwood. Treatise on Petroleum. Griffin.  
 Thompson and Redwood. Handbook on Petroleum. Griffin.  
 Tinkler and Challenger. Chemistry of Petroleum. Crosby-Lockwood.  
 Westcott. Handbook on Natural Gas. Spon.  
 Young. Fractional Distillation. Macmillan.

*Note.* A Bibliography of works on Petroleum (to 1913) is to be found at the end of Vol. III. of Sir Boverton Redwood's Treatise.

*Centigrade degrees equivalent to Fahrenheit.*

| Fahr. | Cent. | Fahr. | Cent.  | Fahr. | Cent.  | Fahr. | Cent.  |
|-------|-------|-------|--------|-------|--------|-------|--------|
| 0     | 17-8  | 54    | + 12-2 | 107   | + 41-7 | 160   | + 71-1 |
| 1     | 17-2  | 55    | 12-8   | 108   | 42-2   | 161   | 71-7   |
| 2     | 16-7  | 56    | 13-3   | 109   | 42-8   | 162   | 72-2   |
| 3     | 16-1  | 57    | 13-9   | 110   | 43-3   | 163   | 72-8   |
| 4     | 15-6  | 58    | 14-4   | 111   | 43-9   | 164   | 73-3   |
| 5     | 15-0  | 59    | 15-0   | 112   | 44-4   | 165   | 73-9   |
| 6     | 14-4  | 60    | 15-6   | 113   | 45-0   | 166   | 74-4   |
| 7     | 13-9  | 61    | 16-1   | 114   | 45-6   | 167   | 75-0   |
| 8     | 13-3  | 62    | 16-7   | 115   | 46-1   | 168   | 75-6   |
| 9     | 12-8  | 63    | 17-2   | 116   | 46-7   | 169   | 76-1   |
| 10    | 12-2  | 64    | 17-8   | 117   | 47-2   | 170   | 76-7   |
| 11    | 11-7  | 65    | 18-3   | 118   | 47-8   | 171   | 77-2   |
| 12    | 11-1  | 66    | 18-9   | 119   | 48-3   | 172   | 77-8   |
| 13    | 10-6  | 67    | 19-4   | 120   | 48-9   | 173   | 78-3   |
| 14    | 10-0  | 68    | 20-0   | 121   | 49-4   | 174   | 78-9   |
| 15    | 9-4   | 69    | 20-6   | 122   | 50-0   | 175   | 79-4   |
| 16    | 8-9   | 70    | 21-1   | 123   | 50-6   | 176   | 80-0   |
| 17    | 8-3   | 71    | 21-7   | 124   | 51-1   | 177   | 80-6   |
| 18    | 7-8   | 72    | 22-2   | 125   | 51-7   | 178   | 81-1   |
| 19    | 7-2   | 73    | 22-8   | 126   | 52-2   | 179   | 81-7   |
| 20    | 6-7   | 74    | 23-3   | 127   | 52-8   | 180   | 82-2   |
| 21    | 6-1   | 75    | 23-9   | 128   | 53-3   | 181   | 82-8   |
| 22    | 5-6   | 76    | 24-4   | 129   | 53-9   | 182   | 83-3   |
| 23    | 5-0   | 77    | 25-0   | 130   | 54-4   | 183   | 83-9   |
| 24    | 4-4   | 78    | 25-6   | 131   | 55-0   | 184   | 84-4   |
| 25    | 3-9   | 79    | 26-1   | 132   | 55-6   | 185   | 85-0   |
| 26    | 3-3   | 80    | 26-7   | 133   | 56-1   | 186   | 85-6   |
| 27    | 2-8   | 81    | 27-2   | 134   | 56-7   | 187   | 86-1   |
| 28    | 2-2   | 82    | 27-8   | 135   | 57-2   | 188   | 86-7   |
| 29    | 1-7   | 83    | 28-3   | 136   | 57-8   | 189   | 87-2   |
| 30    | 1-1   | 84    | 28-9   | 137   | 58-3   | 190   | 87-8   |
| 31    | 0-6   | 85    | 29-4   | 138   | 58-9   | 191   | 88-3   |
| 32    | 0-0   | 86    | 30-0   | 139   | 59-4   | 192   | 88-9   |
| 33    | 0-6   | 87    | 30-6   | 140   | 60-0   | 193   | 89-4   |
| 34    | 1-1   | 88    | 31-1   | 141   | 60-6   | 194   | 90-0   |
| 35    | 1-7   | 89    | 31-7   | 142   | 61-1   | 195   | 90-6   |
| 36    | 2-2   | 90    | 32-2   | 143   | 61-7   | 196   | 91-1   |
| 37    | 2-8   | 91    | 32-8   | 144   | 62-2   | 197   | 91-7   |
| 38    | 3-3   | 92    | 33-3   | 145   | 62-8   | 198   | 92-2   |
| 39    | 3-9   | 93    | 33-9   | 146   | 63-3   | 199   | 92-8   |
| 40    | 4-4   | 94    | 34-4   | 147   | 63-9   | 200   | 93-3   |
| 41    | 5-0   | 95    | 35-0   | 148   | 64-4   | 201   | 93-9   |
| 42    | 5-6   | 96    | 35-6   | 149   | 65-0   | 202   | 94-4   |
| 43    | 6-1   | 97    | 36-1   | 150   | 65-6   | 203   | 95-0   |
| 44    | 6-7   | 98    | 36-7   | 151   | 66-1   | 204   | 95-6   |
| 45    | 7-2   | 99    | 37-2   | 152   | 66-7   | 205   | 96-1   |
| 46    | 7-8   | 100   | 37-8   | 153   | 67-2   | 206   | 96-7   |
| 47    | 8-3   | 101   | 38-3   | 154   | 67-8   | 207   | 97-2   |
| 48    | 8-9   | 102   | 38-9   | 155   | 68-3   | 208   | 97-8   |
| 49    | 9-4   | 103   | 39-4   | 156   | 68-9   | 209   | 98-3   |
| 50    | 10-0  | 104   | 40-0   | 157   | 69-4   | 210   | 98-9   |
| 51    | 10-6  | 105   | 40-6   | 158   | 70-0   | 211   | 99-4   |
| 52    | 11-1  | 106   | 41-1   | 159   | 70-6   | 212   | 100-0  |
| 53    | 11-7  |       |        |       |        |       |        |

TABLE XXVII.

*Fahrenheit degrees equivalent to Centigrade.*

| Cent. | Fahr.  | Cent. | Fahr.  | Cent. | Fahr.   |
|-------|--------|-------|--------|-------|---------|
| - 40  | - 40.0 | + 7   | + 44.6 | + 54  | + 129.2 |
| 39    | 38.2   | 8     | 46.4   | 55    | 131.0   |
| 38    | 36.4   | 9     | 48.2   | 56    | 132.8   |
| 37    | 34.6   | 10    | 50.0   | 57    | 134.6   |
| 36    | 32.8   | 11    | 51.8   | 58    | 136.4   |
| 35    | 31.0   | 12    | 53.6   | 59    | 138.2   |
| 34    | 29.2   | 13    | 55.4   | 60    | 140.0   |
| 33    | 27.4   | 14    | 57.2   | 61    | 141.8   |
| 32    | 25.6   | 15    | 59.0   | 62    | 143.6   |
| 31    | 23.8   | 16    | 60.8   | 63    | 145.4   |
| 30    | 22.0   | 17    | 62.6   | 64    | 147.2   |
| 29    | 20.2   | 18    | 64.4   | 65    | 149.0   |
| 28    | 18.4   | 19    | 66.2   | 66    | 150.8   |
| 27    | 16.6   | 20    | 68.0   | 67    | 152.6   |
| 26    | 14.8   | 21    | 69.8   | 68    | 154.4   |
| 25    | 13.0   | 22    | 71.6   | 69    | 156.2   |
| 24    | 11.2   | 23    | 73.4   | 70    | 158.0   |
| 23    | 9.4    | 24    | 75.2   | 71    | 159.8   |
| 22    | 7.6    | 25    | 77.0   | 72    | 161.6   |
| 21    | 5.8    | 26    | 78.8   | 73    | 163.4   |
| 20    | 4.0    | 27    | 80.6   | 74    | 165.2   |
| 19    | 2.2    | 28    | 82.4   | 75    | 167.0   |
| 18    | 0.4    | 29    | 84.2   | 76    | 168.8   |
| 17    | + 1.4  | 30    | 86.0   | 77    | 170.6   |
| 16    | 3.2    | 31    | 87.8   | 78    | 172.4   |
| 15    | 5.0    | 32    | 89.6   | 79    | 174.2   |
| 14    | 6.8    | 33    | 91.4   | 80    | 176.0   |
| 13    | 8.6    | 34    | 93.2   | 81    | 177.8   |
| 12    | 10.4   | 35    | 95.0   | 82    | 179.6   |
| 11    | 12.2   | 36    | 96.8   | 83    | 181.4   |
| 10    | 14.0   | 37    | 98.6   | 84    | 183.2   |
| 9     | 15.8   | 38    | 100.4  | 85    | 185.0   |
| 8     | 17.6   | 39    | 102.2  | 86    | 186.8   |
| 7     | 19.4   | 40    | 104.0  | 87    | 188.6   |
| 6     | 21.2   | 41    | 105.8  | 88    | 190.4   |
| 5     | 23.0   | 42    | 107.6  | 89    | 192.2   |
| 4     | 24.8   | 43    | 109.4  | 90    | 194.0   |
| 3     | 26.6   | 44    | 111.2  | 91    | 195.8   |
| 2     | 28.4   | 45    | 113.0  | 92    | 197.6   |
| 1     | 30.2   | 46    | 114.8  | 93    | 199.4   |
| 0     | 32.0   | 47    | 116.6  | 94    | 201.2   |
| + 1   | 33.8   | 48    | 118.4  | 95    | 203.0   |
| 2     | 35.6   | 49    | 120.2  | 96    | 204.8   |
| 3     | 37.4   | 50    | 122.0  | 97    | 206.6   |
| 4     | 39.2   | 51    | 123.8  | 98    | 208.4   |
| 5     | 41.0   | 52    | 125.6  | 99    | 210.2   |
| 6     | 42.8   | 53    | 127.4  | 100   | 212.0   |

$$F. = \frac{9}{5} C. + 32.$$

TABLE XXVIII.

| Barometric heights in millimeters of mercury at 0° C. | Boiling-point of water in degrees Centigrade |
|---|--|
| 680 mm.   | 96.91° C.                                    |
| 685   | 97.11  |
| 690   | 97.32  |
| 695   | 97.52  |
| 700   | 97.71  |
| 705   | 97.91  |
| 710   | 98.11  |
| 715   | 98.30  |
| 720   | 98.49  |
| 725   | 98.69  |
| 730   | 98.88  |
| 735   | 99.07  |
| 740   | 99.25  |
| 745   | 99.44  |
| 750   | 99.63  |
| 755   | 99.81  |
| 760   | 100.00                                       |
| 765   | 100.18                                       |
| 770   | 100.37                                       |
| 775   | 100.55                                       |
| 780   | 100.73                                       |
| 785   | 100.91                                       |

TABLE XXIX.

*Calorific value conversion table.*

| British thermal unit (B.th.u.) | Large calorie (Ca.) | Small calorie (ca.) | Pound Centigrade unit (Lb.c.u.) |
|--------------------------------|---------------------|---------------------|---------------------------------|
| 1                              | 0.252               | 252                 | 0.555                           |
| 3.9682                         | 1                   | 1000                | 2.2046                          |
| 0.003968                       | 0.001               | 1                   | 0.002046                        |
| 1.8                            | 0.4536              | 453.6               | 1                               |

The thermal units may be defined as the quantity of heat required to raise the temperature of a given mass of pure water as follows:

|         |             |                                   |
|---------|-------------|-----------------------------------|
| B.th.u. | 1 lb. water | through 1° F. (British).          |
| Ca.     | 1 kilogram  | „ 1° C. (French).                 |
| ca.     | 1 gram      | from 0° C. to 1° C. (scientific). |
| Lb.c.u. | 1 lb.       | „ 0° C. to 1° C.                  |



TABLE XXX.

*Comparative table of characteristics of Asphaltic-base and Paraffin-base Oils.*

| Characteristics                          | Paraffin-base  | Asphaltic-base |
|--|--|----------------|
| Specific gravity for given boiling-point | low  | high           |
| Flash point                              | low  | high           |
| Percentage benzine                       | high   | low            |
| Tar test                                 | low  | high           |
| Cold test                                | high   | low            |
| —  | Decrease of viscosity with rise of temperature less marked than with asphaltic | —              |

*Note.* It must be understood, of course, that the above table is only a very rough guide that would apply to oils characteristically either of asphaltic or paraffin base. The many intermediate oils, so-called, asphaltic-paraffin oils, show no particular indications of belonging to either category.

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